



TAMPERE UNIVERSITY OF TECHNOLOGY

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THE INFLUENCE OF SURFACE TREATMENT ON THE
POLYOLEFIN COATING

Master of Science Thesis

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ABSTRACT

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Low-density polyethylene (LDPE) and polypropylene (PP) are widely used polymers in packaging industry. These polymers differ to one and other by their polymer structures: LDPE has long branched body, when PP is a linear polymer. Branched structure gives LDPE flexibility that PP lacks due to its high level of crystallization. The aim of this research was to compare these polymers in extrusion coating and find out if there are certain procedures in surface treatments that could improve PP's properties in post-coating stage. For instance PP has high melting temperature and low surface energy that prevents its use in extrusion coating.

In extrusion coating a thin film of the molten polymer is extruded through a flat die and then pressed towards the substrate. The substrate in this study was paper and the studied treatments were flame, corona, and plasma focusing on heat sealing, hot tack, surface energy and water vapour transmission (WVTR). The study was divided into four different case studies: 1. The effect of flame treatment, 2. The barrier effect of plasma and corona, 3. The effect of the treatment combination, 4. The influence of time and conditions.

In the results, it was shown that PP has better water vapour transfer resistance throughout the study points and in comparison to LDPE it also reacted more on the surface treatments in case of WVTR. LDPE had higher surface energy in nearly every study point despite the surface treatment and its reaction on treatments was greater. LDPE's and PP's heat sealability temperatures were relatively close to each other in treated study points, though LDPE's reference value was remarkably lower. If flame treatment is combined with plasma or corona, the best results for both used polymers took place in the treatment order where the flame treatment was performed first: sealing temperature, surface energy and WVTR enhanced. In the study of time condition contact angles grow in logarithmic scale in both studied polymers and the highest growth happens in hotter and humid conditions. LDPE's and PP's sealing temperatures follow relatively similar curve in function of time.

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Alhaisen tiheyden omaava polyetyleni (LDPE) ja polypropeeni (PP) ovat pakkausteollisuudessa laajasti käytettyjä polymeerejä, joiden ominaisuudet eroavat toisistaan polymeerirakenteensa vuoksi: LDPE:n rakenne on pitkä ja haaroittunut, PP:n lineaarinen. Rakenteen haaroittuneisuus tekee LDPE:stä joustavan, johon kiteisyysasteeltaan korkea PP ei kykene. Tämän tutkimuksen tarkoituksena oli vertailla näitä polymeerejä ekstruusiopäällystyksessä ja etsiä erityisesti PP:n ominaisuuksia parantavia pintakäsittelyparametreja. PP:n huonoja ominaisuuksia ovat korkea saumautuvuuslämpötila ja alhainen pintaenergia.

Ekstruusiopäällystyksessä ohut sulatettu polymeerifilmi johdetaan rakosuuttimen kautta päällystettävälle pinnalle. Tässä työssä päällystettävänä pintana oli paperi ja tutkitut pintakäsittelymenetelmät olivat liekki-, korona- ja plasmakäsittely. Tärkeimpiä tutkittavia ominaisuuksia oli vesihöyryn läpäisy, pintaenergia ja kuumasaumautuvuus. Tutkimus jaettiin neljään eri osaan: Case 1. Liekkikäsittelyn vaikutus, Case 2. Plasman ja koronan vaikutus barrieriin, Case 3. Pintakäsittelyjärjestyksen vaikutus, Case 4. Ajan ja olosuhteiden vaikutus.

Tulokset vahvistivat käsitystä PP:n hyvästä vesihöyryn läpäisemättömyydestä verrattuna LDPE:en. PP saavutti kaikissa koepisteissä LDPE:tä parempia tuloksia vesihöyryn läpäisemättömyydessä ja se reagoi herkemmin pintakäsittelyyn. LDPE:llä oli miltei jokaisessa koepisteessä parempi pintaenergia ja se reagoi enemmän pintakäsittelyyn. LDPE:n ja PP:n saumautuvuuslämpötilat olivat käsitellyissä koepisteissä suhteellisen lähellä toisiaan, vaikka LDPE:n referenssiarvo olikin huomattavasti alhaisempi. Mikäli liekkikäsittely yhdistetään plasmaan tai koronaan, molemmat polymeerit saavuttavat parhaimmat tulokset liekkikäsittelyn ollessa ensin: saumautuvuuslämpötila, pintaenergia ja vesihöyry-barrier paranevat. Ajan ja olosuhteiden vaikutuksesta kosketuskulmat kasvavat molemmilla polymeereillä logaritmisesti ja suurin kasvu tapahtuu kuumissa ja kosteissa oloissa. Saumautuvuuslämpötilat muuttuvat molemmilla polymeereillä yhdenmukaisesti.

PREFACE

This road has been long and I would like to thank my supervisor Mikko Tuominen for his guidance, patience and help. Also, the laboratory personnel, especially Hilikka and Krista, have been very helpful towards my intention to measure and fail and try again and finally succeed in my studies. I am also grateful for Paul H. Andersson's and Jyrki Vuorinen's help.

My family has been a great support though out my studying time – I hope I can offer some relief by graduating. Special thanks to my parents, Maija-Liisa and Heikki, and also my brother Antti. Studying at TUT has been the best decision I have made so far and therefore, I am grateful for having friends that gave me (probably) the best and craziest years of my life.

Tämä on ollut pitkä matka ja haluan kiittää ohjaajani Mikko Tuomista hänen opastuksestaan, kärsivällisyydestään ja avustaan. Laitoksen laboratoriohenkilökunta, erityisesti Hilikka ja Krista, ovat auttaneet minua suunnattoman paljon pyrkimyksissäni mitata, epäonnistua, yrittää uudestaan ja lopulta onnistua kokeissani. Lisäksi olen kiitollinen Paul H. Anderssonin ja Jyrki Vuorisen avusta.

Perheeni on ollut suuri tuki koko opiskeluaikanani ja toivon valmistumiseni tuovan helpotusta meidän kakkien elämään. Erityiskiitos vanhemmilleni Maija-Liisalle ja Heikille, sekä veljelleni Antille. TTY:lla opiskelu on ollut tähänastisista päätöksistäni paras. Olen erittäin kiitollinen opiskelukavereistani, sillä heidän kanssaan olen kokenut elämäni (luultavasti) parhaimmat ja hulluimmat vuodet.

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ABBREVIATIONS AND NOTATIONS

PE	Polyethylene
LDPE	Low-density polyethylene
LLDPE	Linear Low-density polyethylene
HDPE	High-density polyethylene
PP	Polypropylene
WVTR	Water Vapour Transmission Rate
CAW	Contact Angle Water
IST	Instant Sealing Temperature
GSM	Grams per Square Meter, sample weight
Polymerization	A process of reacting monomer molecules together in a chemical reaction to form three-dimensional networks or polymer chains.
Double bond	A chemical bond between two chemical elements involving four bonding electrons instead of the usual two.
-OH	Hydroxyl, functional group in an alcohol molecule.
-COOH	Carboxyl, functional group consisting of a carbonyl.
Van Der Waals force	Relatively weak electric force that attract neutral molecules to one another.

Cohesive energy	The difference between the average energy of the atoms of a solid (especially crystal) and of the free atoms
Oxidization	Interaction between oxygen molecules and other substances
HNO₃	Nitric acid
CH₄	Methylene
Viscosity	A measure of the resistance of a fluid which is being deformed by either shear or tensile stress.
Surface Tension	Cohesive forces between liquid molecules that resist external force.
Miscibility	A property of liquids to mix in all proportions, forming a homogeneous solution
Solubility	A property of solid, liquid and gaseous chemical substance that forms a homogeneous solution of the solute in solvent.
Lattice	An array of points repeating periodically in three dimensions.

1. INTRODUCTION

Polyolefin plastics are widely used polymers in packaging engineering and their best features are good chemical resistance and formability. The most common polyolefin plastics are polyethylene (PE) and polypropylene (PP), later often has low density polyethylene added to improve the flexibility (i.e. in this thesis' studies). PP has a crystallized structure; therefore it is a hard polymer with poorer processability compared with the low-density polyethylene polymer (LDPE). Most likely PP could regain popularity in multi-layer packaging if its challenging properties would be covered by reasonable solutions. Surface treatments and optimization in treatment parameters could allow new applications for this polymer grade.

Multilayer packaging technology is used due to usability, durability, and barrier properties (water vapour, grease and aroma resistance). A common example of a multilayer packaging material is a milk carton, where the board creates a supporting structure and extruded polymer film seals the package and gives barrier protecting the contained product. The package is environmentally friendly, recyclable, light weight and inexpensive. Therefore, it can replace such materials as glass or plastic containers.

Polyolefin foil properties can be influenced by the surface treatment methods and the main purpose for this thesis is to study these treatments and their parameters. The most common treatment methods used are the flame, plasma and corona. These treatments have significant effect on growth in crystallization and they can change polymer's surface energy. When the level of crystallization grows, the surface becomes harder, thus it will reach better barrier properties. In most cases, the crystallization raises sealing temperature, which sets challenges for packaging technology. When surface treatments change treated surface energy the surface's wettability and adhesion will be improved. As a result, the surface should have better printability: The ink adheres to the surface, and no droplets are formed by surface tension.

The above mentioned treatments have been studied mostly in a coating event, where the adhesion has a significant impact on connecting different layers together. In particular, the morphological effects of surface treatments are still relatively unexplored area on flame treatment, although, the topic has been touched upon in some previous studies. Optimum surface treatments can improve the package with inexpensive and environmentally friendly ways, since the energy consuming properties of the coating can be reduced. At the same time it is possible to reduce chemicals that are used to improve adhesion. Therefore, the goal of this thesis is to study the surface parameters, and surface chemical properties. The main research question is thus: Can these methods improve the usability of LDPE and PP in polymer packaging industry and how will the

time and conditions effect on the polymers surface properties? Basic assumption is that PP is a polymer having properties that could be enhanced to compete with LDPE.

The work of implementation began by test runs, using a variety of set-up parameters and various treatments, mainly focusing on flame treatment. After several test runs, laboratory measurements were carried out, analysing the results of which can be compared to draw conclusions on the properties of plastics and opportunities. The used study points were to investigate four different case studies, where two polymers were under examination: LDPE and PP. The case studies were the following:

Case 1. The effect of flame treatment parameters.

- How the flame parameters are affecting on
 - IST
 - CAW
 - Barrier on LDPE and PP(LDPE)?

Case 2. The barrier effect (water) of flame, corona and atmospheric plasma treatment efficiencies.

What is the influence of treatment efficiency on

- CAW
- Sealability
- Barrier properties of LDPE and PP?

Case 3. The effect of the treatment combination.

What is the effect of treatment order?

- Flame + Corona/Plasma
- Corona/Plasma + Flame

Case 4. The effect of aging and condition of the treatment levels

- What is the influence of time and conditions

The theoretical part deals with the properties of polymers: in particular the morphological characteristics and surface energy theory. The experimental section aims to strengthen the results of earlier studies and examined the effects of surface treatments, in particular the effect of flame treatment on polymer morphology. In addition, research carried out over the impact of treatment.

THEORETICAL PART

2. BACKGROUND

2.1. Polymers in general

Polymers are generally divided into natural polymers and semisynthetic and synthetic polymers. Synthetic polymers include polyolefin plastics (PO) which are the most common thermoplastics, covering up to 50% of the plastics used worldwide. [1]

Most polymers are formed from larger molecules built by carbon, hydrogen or oxygen atoms. Usually “polymer” is used as a word referring reunification of a number of individual parts, i.e. the monomers. The polymer can be formed from one or more monomer grades and chain length can be up to millions of monomer units. Polymers formed by one monomer grade are called homopolymers, which may have linear, branched, or cross linked structure. If the polymers are formed by two or more types of the monomers, they are named copolymers. Polyolefin are the linear and branched hydrocarbons, with at least one double bond. [1, 2]

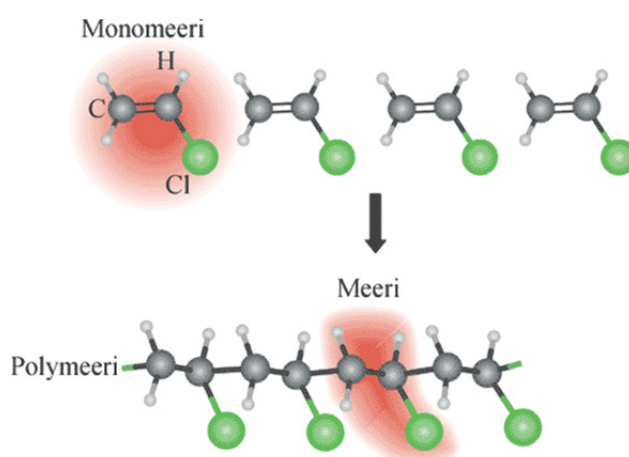


Figure 1. *The formation process of the polymer. [5]*

The polymers can form various structures, such as the ladder, and spiropolymers. The interpenetrating network is mixed with two different polymer nets, which form a net structure of the polymers that do not react with other polymer. The net structure generates by polymerization of the mixture components to bridge cross-link, or by the presence of another polymer net. [2, 3, 4] For example this phenomenon can be seen in properties of PP(LDPE); the polymers mixture is divided by of different melting points creating a net.



Figure 2. *Polymer structures; a) linear-amorphous, b) linear-partially crystallite, c) branched-amorphous, d) severely netted, e) strongly netted, f) linear-ladder. [3]*

Besides branching polymers can have other topologies: linear, network (cross-linked 3D structure), integrated polymer network (IPN), comb, or star as well as dendrimer and hyperbranched structures. [2]

2.2. Binding energies of the polymers

Since polymers consist of large molecules, the bonds between the atoms are mainly covalent. Also the presence of ionic bond is possible if the polymers are carboxyl or other acid groups that are able to react with the metal. Metal bonds, however, do not occur. The main secondary bonds are hydrogen bonding, van der Waals forces, as well as cohesion energy. [2, 3] Although, the secondary bond forces remain relatively low compared to the molecular bonds, they can be influenced by the surface energy. [6]

Hydrogen bond is formed if the hydrogen atom is bound covalently to electro-negative atom, and there is also a negative electrostatic interaction between the atoms. Electron pair bond formation is not divided equally between the atoms hydrogen bonds, so the electro-negative atom (e.g. fluorine or oxygen) becomes more attractive. The hydrogen bridge is strong only on electro-negative substances (e.g. F, Cl, O, and N) and in between hydrogen. For example, -OH, -COOH, NHCO and other strongly polar groups can form hydrogen bonds. Energy of hydrogen bonds is only 5-10% of the energy of the covalent bonds. [2, 3]

Van der Waals dispersion forces have an effect on polymer chains through the non-polar molecules. Also completely non-polar molecules are able to crystallize, thus there are tensile forces between the molecules. All molecules, atoms, nuclei and electrons oscillate in relation to each other, so that each molecule behaves like an oscillating dipole. These instantaneous dipoles induced dipole bonds with neighbouring molecules, and this is the result of a general attraction between the molecules. Dispersion forces

reach the largest values in crystalline regions, because the molecules are as close to each other as possible. [3]

All of the molecules consisting of atoms with differing electro-negativity formed a so-called dressing dipole moment. Permanent dipoles orient themselves relative to one another so that the positive end of the second dipole is approaching another head of the negative dipole. Such molecules form a very weak interaction between. [3, 4]

In reality, polymer chains are always surrounded by neighbouring chains that rise interactions reducing the chain mobility. Secondary bonding effect is called cohesion energy, which is usually calculated per unit volume. The cohesion energy can be defined as the amount of energy required to separate the molecular liquid or solid molecular crowd. The cohesion energy effect of the polymer is shown in the physical parameters such as viscosity, surface tension, friction, miscibility, solubility, and mechanical properties below the glass transition temperature. [3, 4]

2.3. Morphology

In particular, the plastics crystallization is a major factor in applications of polyolefin, as crystallized structure can give properties for strength and chemical resistance. Plastics are often divided according to their crystallinity to amorphous or crystalline grades. Polyolefin in turn, are partially crystalline plastics, because they are composed of amorphous and the crystalline regions (Figure 2.). High molecular weight components are crystallized first at high temperature and are the dominant characteristics of crystals. Similarly, small molecular weight exhibit crystals crystallized later at a lower temperature. [2, 3, 4]

Crystals composed of repetitive units' volume: simple lattice. This is a purely mathematical quantity, i.e. a space formed by a set of points. Crystal consists of flat surfaces and depending on the circumstances that they can evolve differently in various directions. As a result, the crystals may vary enormously, even if the lattice is the same. Despite the diversity of crystal structure, the corresponding surfaces of the angles are always equal. [3] The crystal's structure is repeated on a regular basis in every direction, and therefore identical atoms or molecules are located in regular distance from each other. A lattice usually contains 1-8 molecules and the crystals are usually divided into an external review of the following: triclinic, monoclinic, orthorhombic, tetragonal, hexagonal, rhombic and cubic crystallite system. The order of the mentioned systems is based on the growth of symmetry. The lattice size and shape of each substance has characteristic feature, which can be utilized to identify the substance. [2, 3]

Polymer chains compaction to crystals occurs between the adjacent chains of the same chain or in interaction between different parts of the same chain. Chains between the secondary bindings take place and the van der Waals -or hydrogen bonds through

the covalent potential have been used to commit the body to form the chain. As a result, the polymer crystals are anisotropic, without exception. Due to the length and the symmetry relations the polymers often crystallize as rhombic or monoclinic lattice.

Polymer chain compaction to polymer crystal follows three rules:

1. The chains retain certain conformation state in the crystal (the lowest value of the internal energy)
2. The chains are placed as tight as possible to one and other
3. One particular chain can maintain its symmetry qualities as far as possible. [3]

Crystallization of polymers limits the different bond energies of the chains in the direction as well as against them, together with lengthy and potentially asymmetric chains. In addition, large side groups can completely prevent crystallization, the material is completely amorphous. Amorphous material is un-organized; even in the form of solid, liquid form of the viscosity is very high. Every solid substance has a characteristic crystalline form. [2,3]

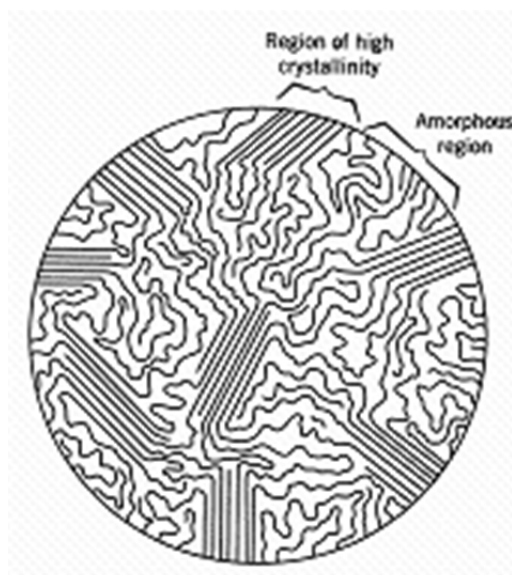


Figure 3. Polymer showing regions of crystallinity and amorphous regions [33]

When crystallized structure from molten polymer form, the disorganized crystals changes to organized crystals forming lamellae and crystal lamella stacks. Shape of the crystallized structure formed from the molten state depends largely on the molecular weight, chain branching and crystallization temperature. Components with high molecular mass crystallize at higher temperatures and correspondingly lower mass components at lower temperatures. Small and large molecular components diverge to distinct crystal structures. [1, 3]

The most common factors to increase crystallite are the symmetry of the molecular structure, high crystallization temperature and slow cooling. Chain orientation is also an increasing factor. Usually polymer molecules orientate themselves along the molten mass flow direction, so in extrusion coating machine direction orientation is almost certain because the tension is maintained in the track even after the molten has cooled down. Crystallization increases tensile strength, stiffness and hardness. Increasing the degree of crystallinity also increases density, stress cracking, shrinkage and bending of the sample's shape. On the other hand a high degree of crystallisation will improve chemical resistance. Similarly, the degree of crystallinity decreases when molecular structure is branched and molecular weight is greater. [1, 3]

2.4. Polyethylene

Polyethylene (PE) is a partially crystalline polyolefin grade, which has a wax-like surface and the formed thin films are transparent. One of its best features is excellent chemical resistance; Polyethylene is resistant to water, salt solutions, dilute acids and alkalis. In addition, it is a good electrical insulator. At room temperature polyethylene is not soluble in well known solvents, but it reacts with strong acids such as HNO_3 . One of PE's advantages is also a good formability and processability. When polyethylene is heated, it first melts and then starts to decompose at 290°C or above. The most suitable processing temperature range is thus $220\text{--}310^\circ\text{C}$ range. More than 350°C , it begins to form volatile substances. [1, 2, 21]

Polyethylene polymers are divided into three main commercial categories by their manufacturing processes and properties:

HDPE	High density polyethylene, linear chain.
LDPE	Low density polyethylene, short and long branches.
LLDPE	Linear low density polyethylene, short branches.

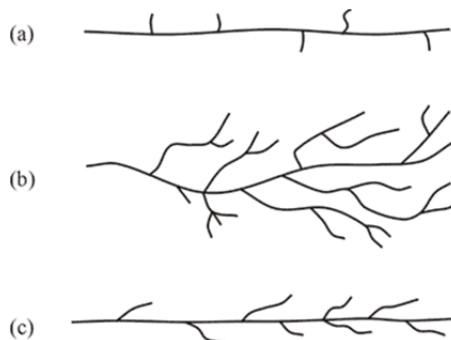


Figure 4. Chains of polyethylene: a)HDPE, b)LDPE, c) LLDPE. [6]

The polyethylene type this thesis focuses on, is LDPE, which is the most used type of polyethylene in packaging technology and other industries. Since the beginning of commercial manufacture, LDPE has been the primary resin for extrusion coatings. Even these days, LDPE covers 86 % of Western Europe resin consumption in 2005. [19] Due to its short branches, LDPE crystallinity rate reaches only 50-60%. Low degree of crystallinity leads to a lower melting point when compared with the linear polyethylene. Wide distribution of the molar weight and the long side chains make LDPE easily formable and a flexible polymer. LDPE films are relatively transparent and thus very suitable for films and coatings. However, LDPE's characteristics of strength are weaker compared with linear low density polyethylene (LLDPE). [1, 2, 6,]

2.5. Polypropylene

Polypropylene is the third most used polymer grade in plastics industry after polyethylene and polyvinyl alcohol. Polypropylene is produced from petroleum refining by-product propylene by polymerization. [3] In most cases in paper converting technology, PP has added some LDPE, the film should then be a little more flexible and the processability improves. Polypropylene has closely similar characteristics with high density polyethylene. PP's melting temperature (160-175 C) and glazing point (-20 ... -10) are, however, somewhat higher than those of polyethylene. The mechanical properties and crystallization of polypropylene depend on the size of molecules. [1,2, 6, 16]

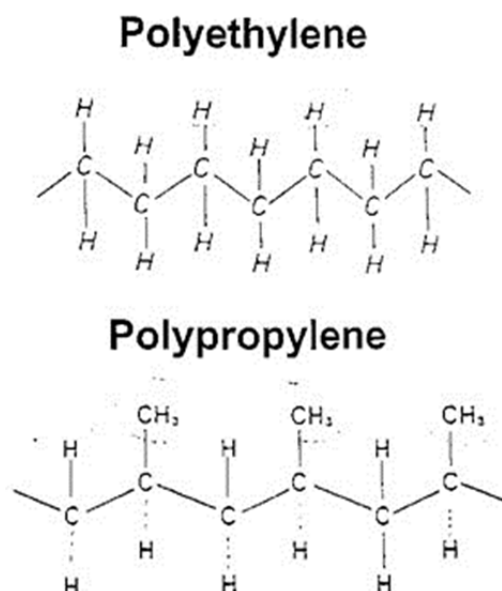


Figure 5. The polymer structures of PE and PP. [32]

Polypropylene crystallinity is affected by the methyl's (CH₃) location in the structure of the space. If the methyl group located on the same side of the polymer

chain, it is isotactic, i.e. crystalline, chemically-resistant PP. This type of PP is the most common: over 90% of the commercial polymers belong to that group. Correspondingly, on atactic polymer the methyl molecules are located randomly on a polymer chain above and below. Atactic polymer is a crystallized polymer and its heat resistance is poor. The syndiotactic polymers have alternating chain methyl group above and below the polymer chain. [2, 3, 6]

2.6. Barrier Properties

Polyolefin plastics are known to have good barrier properties, i.e. the ability to prevent vapour, flavour and grease penetration. Also, permeability, timeliness and workability guarantee their widespread use for example in the food packaging industry. The packaging industry has a growing need to use more environmentally friendly, water-soluble inks, whose adhesion to polyolefin surface is challenging. For this reason, the research of surface energy and adhesion has gained increasingly significant role. [4, 6]

The barrier properties are affected by crystallization, environment, temperature, surface area of chain orientation, and the stiffness of the material thickness. Compared with metals and glass, plastics have higher permeability in the case of some substances. Polar substances, such as water and alcohol pass more easily polar plastics, but the non-polar plastics such as PE and PP are highly resistant for these substances. The situation is the opposite with polar gases such as oxygen and nitrogen. The permeability almost has a linear relationship between the plastic layer and material thickness. Also, the density has a significant impact on permeability. [4, 6, 7, 22]

Inside the substance, molecules are in a different state than on the surface as inside the molecules' attraction forces are equal to the repulsion forces: molecules on the surface have power towards the substance. Since this power tends to reduce the material surface, the phenomenon consists of opposing power: the surface tension. With solids, the term for describing this event is usually the surface energy and with fluids the surface tension. Therefore, to obtain the ink to seize the coating, the surface energy must be greater than the corresponding ink. [2, 8, 13]

2.7. The Surface Energy and Adhesion

Adhesion refers to the power which is composed between two different interfaces. These energies encounter their persuasion; Interactions may be formed by atoms, molecules and ions. Interfaces between the chemical properties usually dictate the event. Adhesion phenomenon is divided into mechanical and chemical parts. Mechanical locking is influenced by surface roughness and material absorption. For example, when paper or board is coated by extrusion method, molten polymers flow into holes between the fibres to form a structure where the final attachment will happen

after the surface cools down. Mechanical locking is more challenging with smooth materials with low surface energy, such as ink adhesion to the polymer surface. Chemical adhesion in turn, happens at the molecular level. As a result, printing ink and sticking to the surface of the polymer can be provided by surface treatments or chemicals. [4, 18, 13]

Although, the secondary dressing forces are relatively low comparison with the molecular affinities, for example, they can be influenced by the surface energy and hence the surface adhesion.[15]

Usually the main purpose for the surface treatment is to influence the course of surface energy and then contribute to the film's commitment to the track, but also to the surface adhesion of the film i. e. printing event. Adhesion contributes significantly to the polymer melting temperature and viscosity of the coating speed and coating thickness. The bottom line is that the polymer's chemical compatibility with the surface is important factor for adhesion by trough the surface chemistry and functional groups. Mechanical adhesion affects the track surface roughness, because the rough surface to adhere to a larger area and allows the flow of polymer microspores. [4, 7, 20]

In extrusion event, the track surface can be treated before the coating event, then the polymer surface adheres better to the track. This procedure is possible to do after the coating, so that for example, printing ink adhesion to the surface of the polymer is improved. Surface treatment methods used are the flame and corona, which allow the artificial increase of surface energy. As a result, coating or printing ink surface to be wetted at the molecular level. The corona is the most common of the surface preparation methods. The process uses high-frequency and high-voltage alternating current in order to oxidize the surface, thereby increasing the surface energy and improving the adhesion. Changes in the surface are of the chemical, physical and electrical properties. [1, 6, 7]

When used as a post-processing, the flame changes the chemical composition of the polyolefin surface so that the molecules cross-link and chains are being formed. Changes in the surface are both morphological and topographical. Longer polymer chains break apart and microstructural coarsening occurs. Post-processing can also be used to modify coating's weak bonds stronger. Treatment affects the surface to become activated and micro-etched. Advantageously the surface is cleaned and the fibres causing micro-holes are burned off. Using the flame for post-processing has side effects like deterioration of the surface properties, dimming and scratching. [6, 7, 20]

Both Corona and the flame treatment have also the advantage of water evaporation, surface oxidation and the track warming (adhesion). The advantage of these methods is also limited area of affection: polymer surface can be treated without affecting the fluffiness of the bottom, i.e. bulk. [4, 6, 7]

2.8. Heat sealability and hot tack

One of the most important features for polyolefin in packaging industry is the heat sealability: the packaging is as reliable as its weakest point, as the leaking seals negligible the other properties of the coating. The idea of heat sealing is to connect two olefin-based surfaces by the effect of heat, pressure and time. In the sealing event there are two heated Teflon jaws that press the surfaces together (Figure 6) In the sealing event the polymer chain will create new linkages, and when it cools down the seal is crystallized into its final form. The best heat sealing polymers have a wide 'sealing window. Also the sealability in low temperature is an advantage in the modern packaging technology requirements. [8, 9, 19]

In the sealing process partially crystalline polymers melt and the pressure increases molecular contacts on the surface of the melt film. Sufficiently long sealing time leads to cross-binding and thus forms strong bonds. The strength of the seal is best when the plastic is melted completely because the amorphously organized chains get mixed and the seam between the interfaces does not contain already crystallized areas. When the surface tension is on lower level, the sealing can happen in lower temperature. [9, 10, 28]



Figure 6. *Heat seal procedure: Extrude coated surfaces melt between the Teflon jaws and form a seal. [29]*

Hot Tack is a word describing the strength of a hot seal during the first 500 to 1000 milliseconds after the sealing jaws opens away from the film. The strength of a seal changes quickly after the seal cools. Therefore, hot tack is a variable that is a function of time and of ambient cooling conditions. As an effect, heat transfers from the seal to its environment. [27, 28]

Hot Tack is important mainly in the converting operations where product is dropped into a package shortly after the seals have been made. The most frequent occurrences are the sealing of carton end flaps on high-speed folding carton filling or in the gable top of a liquid carton. In sealant film selection it is important to notice the weight of the product and force at which the product would be coming in contact with the molten polymer seal. Polyethylene films can be designed to have specific hot tack properties that match up well with the converting method employed. The thickness of the coating and surface treatments can have significant effect on hot tack. [27, 28]

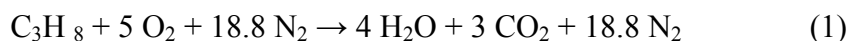
3. SURFACE TREATMENT METHODS

Polyolefin coating gives paper and cardboard essential benefits, such as water-, gas-, grease- and flavour-barrier. Heat sealability, hot tack, good adhesion properties and printability are major factors for packaging process. These properties can be improved by surface treatment methods.

The most common methods of surface treatment of polyolefin coating are flame, corona or plasma. These treatments are intended, e.g. to increase the surface polarization and oxidation as well as to improve the adhesion and barrier properties by modifying the polymer chain into the desired shape. Post-processing aims to create certain functional groups to the surface of polyethylene: as a result the surface energy increases and the cross-linking of the polymer chains increases. Also the surface crystallization and roughness increases due to morphological changes.

3.1. Flame

The idea of the flame treatment is to raise the surface oxidation and therefore improve the surface energy. This treatment increases wettability and improves adhesion properties. The flame treatment can be performed either before the extrusion when adhesion of the extrusion coating to the base track improves or as a post-processing, as in this study, to improve print colour adhesion. In the flame process track is targeted near flame with required parameters. The gas used in the process is usually methane (CH₄), propane (C₃H₈) or butane (C₄H₁₀). [6, 7,] Flame reaction results formation of water, carbon dioxide, and nitrogen:



When used as a post-processing the flame changes the chemical composition of the polyolefin surface so that the molecules get cross-linked and chains are being formed. Changes in the surface are both morphological and topographical. Longer polymer chains break apart and micro-coursing occurs. This also modifies weak bonds of coating stronger. The advantage of this method is that the plastic surface can be modified without affecting the fluffiness of the base paper, i.e. bulk. Treatment affects the surface also to become activated and micro-etched. Furthermore the surface gets cleaner, active and micro-etched. Negative side effects are deterioration of the surface properties, dimming and scratching. [6, 7]

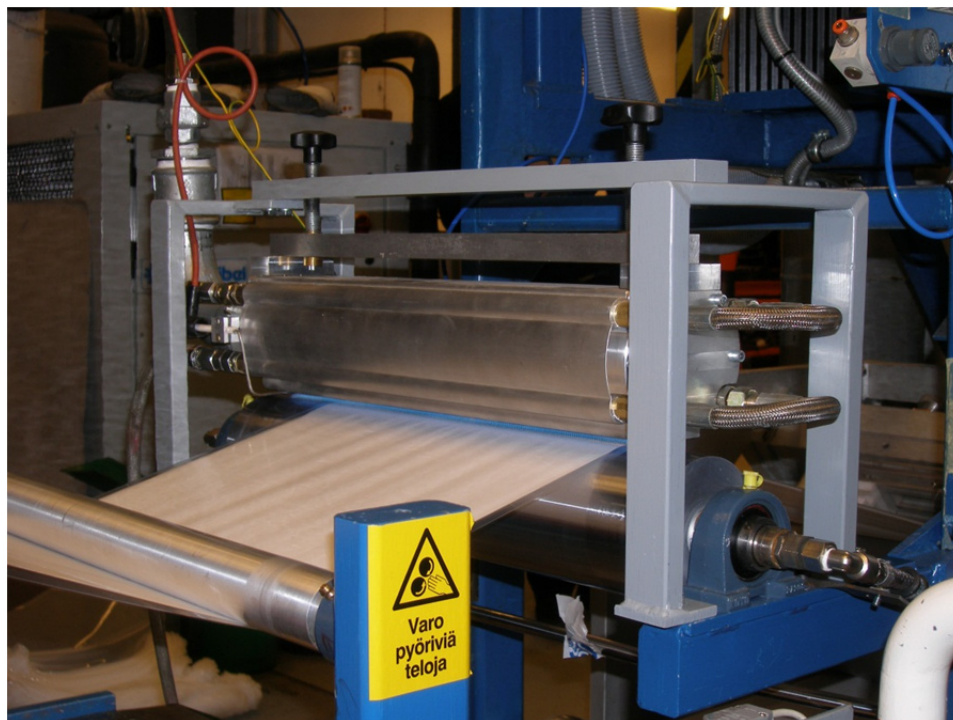


Figure 5. *Flame treatment.*

The process consists of the flame generated from air-gas mixture guided at the desired distance towards the track. The paper path runs through the flame guided by the cooling cylinder. The flame treatment must be carried out smoothly and uniformly. Treatment system consists of a gas- and air-supply system, gas mixing system, and machine wide burner over the track which can handle entire track at a time. [6, 15]

The main parameters of the flame treatment are the gas feed rate, air-gas ratio, the track distance from the flame and the line speed, i.e. the duration of treatment per area. The gas feed rate is the amount of air-gas mixture flow to the burner. The flame structure or temperature does not change as the mass flow rate increases, but it is expanded and the thermal capacity changes.

3.2. Corona

The corona is the most common method of surface treatment. Treatment uses high-frequency and -voltage alternating current to oxidize the surface, thereby increasing the surface energy and improving the adhesion. Corona eruption causes changes in the chemical, physical and electrical properties of the surface (Figure 7). [6, 7]

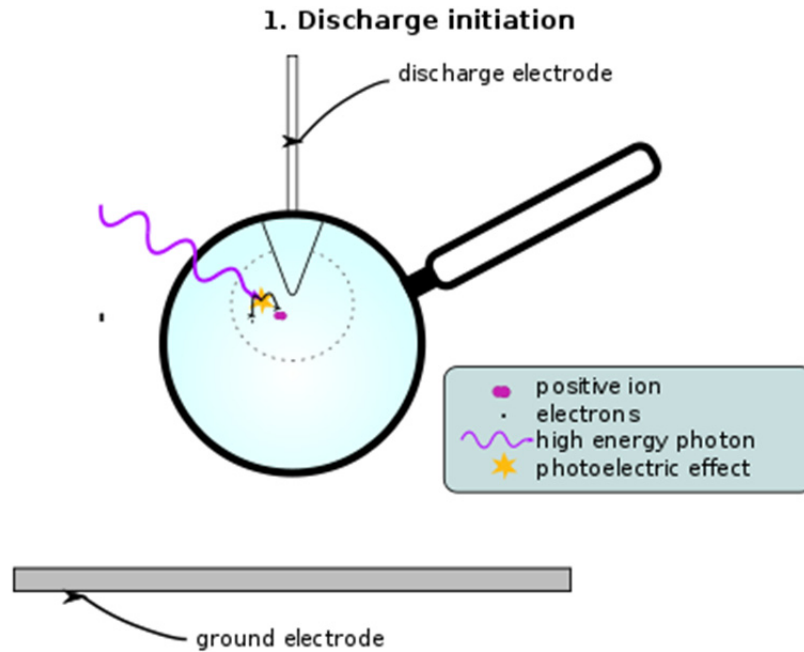


Figure 6. Corona eruption. [31]

In a corona process the current develops an electrode with high potential in neutral fluid, usually air, and ionize it. As a result there will be plasma around the electrode. Eventually, the ions pass charge to the areas of lower potential, also neutral gas molecules can be formed by recombination. Both corona and plasma treatments use high voltage to ionize air or gas. [6, 14]

3.3. Plasma

Plasma, the fourth state of matter, refers to a substance, which consists of more than 99% of the total matter of the universe. Plasma is a partially or fully ionized gas with electrons, positively or negatively charged ions and atoms and molecules both excited and in basic state (Figure 8). The plasma modifies the surface by breaking molecular bonds and exposing sites for new chemical bonds.

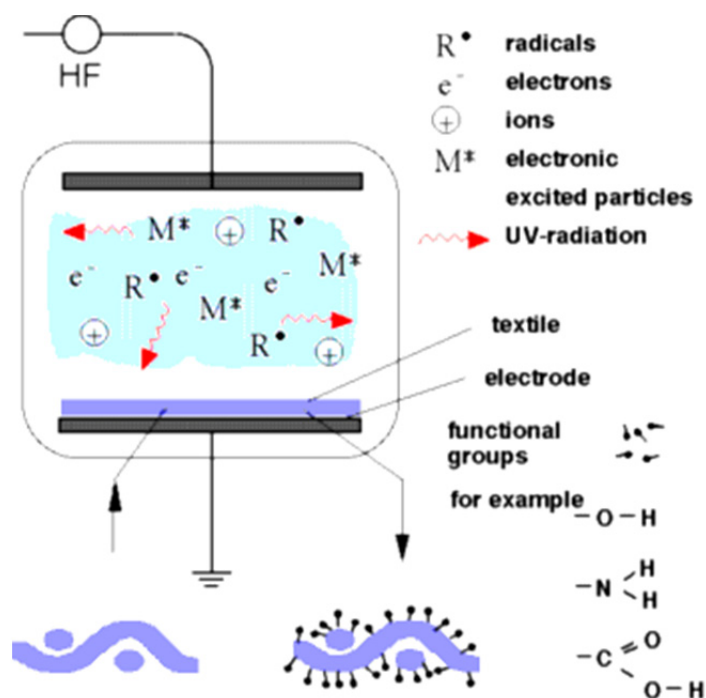


Figure 7. Plasma treatment. [17]

Atmospheric plasma treatment was targeted to be an alternative to the corona, because the corona treatment can be uneven causing micro-holes and as a background treatment it may also cause blocking. Corona's unevenness is due to filament type discharge: discharging consists of small channels (diameter 100 μm), which affect only part of the materials area. Plasma treatment aims to bring about a so-called glow discharge, which is not only smoother, but also more efficient. The perfect glow discharge can only occur in the vacuum, thus the treatment reach the better efficiency and uniformity in comparison to normal open-air plasma treatment. Plasma treatment also has the advantage to not affect the electrical properties of the base, and it binds nitrogen and oxygen to the material surface, which increases the formation of the secondary bonds. [6,7] The plasma treatment can achieve the same level of treatment quality as the corona process about half the amount of power as Juho Lavonen showed in his master's thesis [13]

EXPERIMENTAL PART

4. RESEARCH METHODS AND MATERIAL

The study was carried out by trial runs on TUT's Pilot Line in the department of Energy and Process Engineering in paper converting laboratory. In this line it is possible to carry out surface treatments using the flame, corona and plasma devices. All the test runs were performed by using the same base paper: SwanWhite (UPM). Two different qualities of polymers were used as tests samples: LDPE, PP(LDPE). All the polymers were supplied by Borealis. The samples used in the experiments were pre-coated with the same line, giving similar base for every study point, thus the investigation concentrated purely on the effects of surface treatments on the polymer.

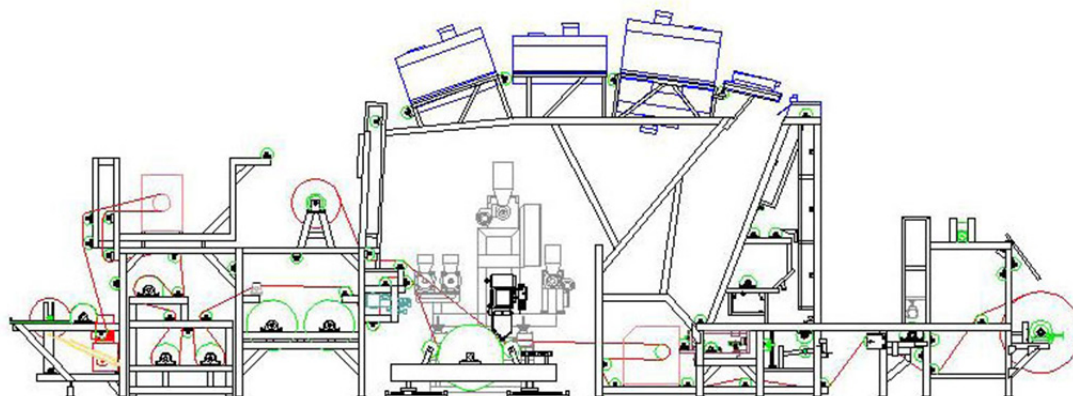


Figure 8. *Pilot-line at Tampere University of Technology. (TUT)*

4.1. Contact angles of water on the surface

There were two different devices used to measure the contact angles: Pocket Goniometer PG-3, and KSV CAM 200, as the first mentioned device was inoperative in later studies. Both measurements are performed in so-called fixed droplet method, which examines the angle between the sample surface and the fallen droplet. The biggest difference between these measurement tools was the sample reading: Pocket Goniometer is a manual device and KSV CAM 200 includes an automatic measuring technology. Both of the devices could use different fluids, such as dimethyl and ethylene glycol, for droplets, but the measurements were carried out with distilled water. Water's contact angle is generally considered to be a suitable way to evaluate the surface energy and wetting caused by surface treatment methods. Liquids contact angles can be determined by the surface energy by the ASTM D 5946 standard, dispersive and the polar component and acid-base interactions based methods. [11, 12]

The contact angle measurements were carried out after the test run, except, in time and condition study these measurements were performed in chosen time. The samples were cut parallel to the track centre of the machine to the test area should be as similar as possible. To prevent possible presence of impurities effecting on the sample, touching were avoided. The used drops size for all measurements was size 4 microliters. PG-3 meter droplets drip into the sample and the transfer is carried out manually, but in the KSV device (Figure 10) these functions and sample analysis is performed automatically after inserting the sample. Drops were instilled into the 7-8 per a study point. Measuring device programs analysed image angles, but manual corrections were performed (if necessary) by setting the real border points of the image.

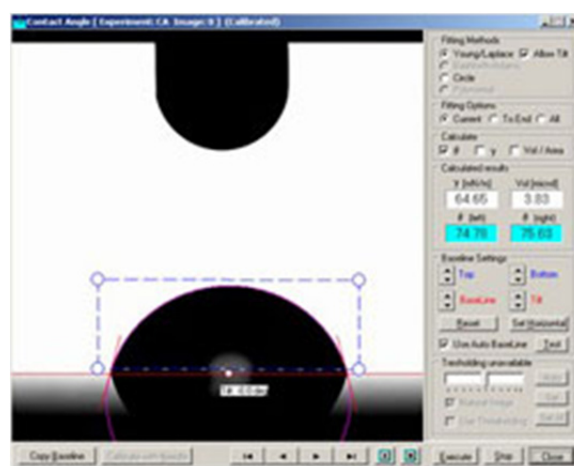


Figure 9. Measuring water droplet on KSV's device. [30]

In some cases the software appliances were not able to find the actual surface or angle due to reflections of light. KSV device's had some challenges in measuring functions compared to PG-3: problematic sample layout of the device, high-contrast images and lack picture modification.

4.2. Water vapour

Water vapour permeation was studied in Water Vapour Transmission Rate method (WVTR). The test is performed by using low and wide aluminium dishes (Figure 11) with the separate upper edge for the wax seal and paper. Bottom of the container contains calcium carbonate salt and it is covered with a round-cut sample which is sealed by the edges with the bee wax-paraffin mixture. During the sealing the centre of the sample is covered with a cylindrical-shaped metal piece and the rest of the sample is covered with molten wax mixture. After the wax has cooled, the cylinder will be

removed. The area without wax is thus 50 mm², the size which enables to calculate the water vapour transmission per surface area.

The water vapour should penetrate only through the sample. Salt tends to absorb water; therefore the water-retention will ensure that the permeated water vapour stays inside the container. Samples are placed in the desired conditions usually for five days. Water vapour absorption can be found out by calculating the sample weight differences every 24 hour. All of the performed WVTR measurements had the same conditions: 38 °C temperature and 90% air humidity. Measurements were carried out by testing five parallel samples per test point. [22]



Figure 10. *Water vapour transmission rate is measured by using aluminium dishes that collect water from the surroundings.*

WVTR method is not completely reliable, as in some cases the wax is not sufficiently tight around the edge of the container and the results get invalidated. However the reliability of the measurement increases if the same test point is measured with increased amount of parallel samples. Although the weighing scale used is accurate (0.0001 g), the weighing requires special care: the results are affected by temperature, air movement and the timing of the weighing scale calibration.

Coating thickness

The thickness of the coating affects to the water vapour permeation, thus treated samples that were to ending up to WVTR were weighed prior to the examination. Weights are scaled proportionally to the mass of the base paper and basing on the difference the amount of the coating on every sample can be figured out. Weighing scale used was 0.0001 g accurate.

4.3. Heat sealability and Hot tack

Experiments were carried out using Kopp SGPE 20 heat-sealer; Teflon coated jaws press two paper strips film sides together. After the joint has cooled down, about a minute later, the seal is ripped open in the longitudinal direction by hand. The test results depend largely on the personal vision: Torn seal quality is evaluated numerically on a scale from zero to five. Zero means non-stick surface and five complete fibre rip. Parameters used for all seal-ability experiments were: seaming time 0.5 s, pressure 200 bar. Seal-ability temperatures ranged from 70-190 C.

Also the Hot tack measurements were performed by Kopp SGPE 20 heat-sealer, by using its automatic sealing force measurement characteristics. Hot tack means the strength the seal has instantly after the sealing event. Usually this measured value is lower than the actual sealing strength as the seal does not have time to cool down and therefore create stronger bonds.

5. RESULTS

In the study measurement point selection, the most significant parameters were surface treatment, number of treatment per track and the process speed. The change of the flame surface properties were studied by changing air-gas ratio, track speed and the amount of the gas flow. Also, the function of track distance from the flame was investigated. On corona, the purpose of the study was to find out if the changes are achieved by electrical discharge power and the track speed. The studied factors for plasma treatment were processing speed and the amount of gas, as well as the efficacy of the eruption.

The aim was to approach the surface treatment effects by case studies. Each study point had one parameter under investigation. Therefore, all the other parameters were held constant. It was possible to see if the studied parameter had any influence on certain properties, such as CAW, IST or barrier.

The case studies were the following:

Case 1. The effect of flame treatment parameters? How do the flame parameters effect on IST, CAW and barrier?

- LDPE and PP(LDPE)

Case 2. The barrier effect (water) of flame, corona and atmospheric plasma treatment efficiencies. What is the influence of treatment efficiency on CAW, sealability and barrier properties of LDPE and PP?

- Flame
- Corona
- Plasma

Case 3. The effect of treatment combination. What is the effect of treatment order?

- Flame + Corona/Plasma or Corona/Plasma + Flame

Case 4. The effect of aging and condition of the treatment levels. What is the influence of time on LDPE and PP on different treatments?

- Contact angles from 24 hours to two months
- Sealing temperatures from 2 hours to six months
- Hot tack strengths from 24 hours to one month
- Conditions being

- 23°C/50 RH
- 25°C/75 RH
- 38°C/90 RH

5.1. The Effect of flame treatment parameters (Case1)

Two different polymer mixtures were investigated: LDPE, PP(LDPE) in the flame treatment test runs. The studied variables were line speed, the air-gas ratio, the flame distance from the track as well as the gas flow. While these variables were investigated the other factors were held constant. Finally, the samples were measured by CAW, WVTR and IST test methods. To ensure that the coating thickness was even, also GSM results were run (the accurate results can be seen in appendices together with other test results).

Table 1. Flame treatment parameters, variables in bold.

Study point	line speed	air-gas ratio	distance	air flow
1	100 m/s	26:1	12 mm	700 m ³ /min
2	200 m/s	26:1	12 mm	700 m ³ /min
3	100 m/s	24:1	12 mm	700 m ³ /min
4	100 m/s	26:1	12 mm	500 m³/min
5	100 m/s	26:1	6 mm	700 m ³ /min
6	ref. untreated			
7	50 m/s	26:1	12 mm	700 m ³ /min
8	75 m/s	26:1	12 mm	700 m ³ /min
9	100 m/s	28:1	12 mm	700 m ³ /min
10	100 m/s	26:1	18 mm	700 m ³ /min

CAW

To find out the level of surface energy the contact angles were measured and to discover how the treatment parameters effect on contact angles the following variables were investigated: track speed, air-gas ratio, distance between the track and the flame, air flow. The measurements were performed by Pocket Goniometer PG-3.

The speed of the track (Figure 12.) in the flame treatment gave relatively linear growth on LDPE's contact angles. The variation and changes between of the study point values were slightly smaller on PP. LDPE's reaction on the flame treatment was stronger as the difference between the reference value and the treated study points were greater. PP's angles were approximately 15° smaller than the reference value and therefore the changes were rather close to the reference. LDPE's contact angles were 20-30° smaller than the reference value; therefore it had higher surface energy in

general when flame treatment was used. As the contact angles on untreated surface were relatively large, the surface energy was correspondingly low. The surface energy increases on the slow track speeds on flame treatment, especially on LDPE. Untreated LDPE and PP did not differ much in their contact angles.

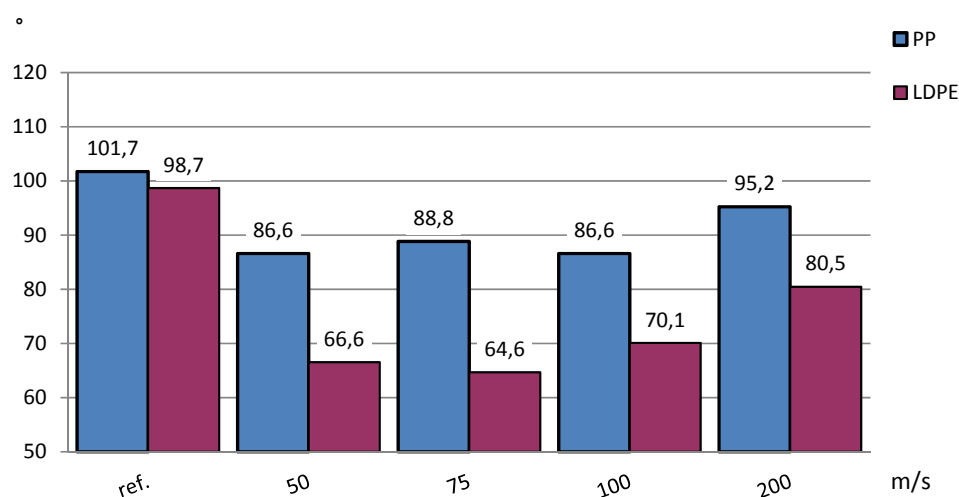


Figure 11. *The influence of the flame treatment's line speed (m/s) on CAW (°).*

In the study of air-gas ratio (Figure 13), it was shown that when the air-gas ratio increases, the contact angles will reduce. The change for PP-grade was relatively linear, but the changes observed were smaller than what LDPE had. Therefore air-gas ratio seemed to create a linear growth in surface energy for both studied polymers, but LDPE had higher surface energy level in general.

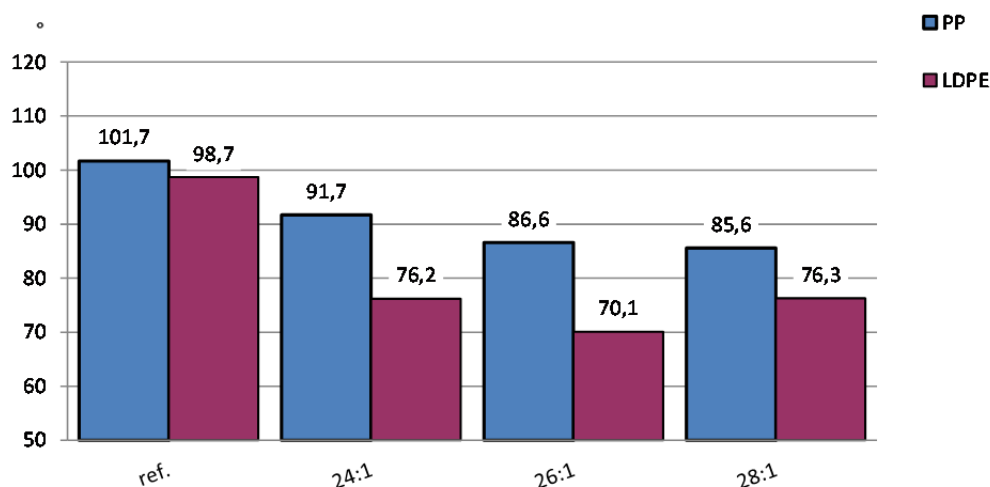


Figure 12. *The influence of air-gas ratio on the flame treated surface's CAW (°).*

In the study of treatment distance (Figure 14), LDPE and PP seemed to have differing values on surface energy. Both polymers received smaller contact angles than the reference point, but PP's values grew when the distance was greater. LDPE had relatively similar results in all distances; the lowest angle was achieved in 12 mm distance, when the lowest value for PP took place in 6 mm distance.

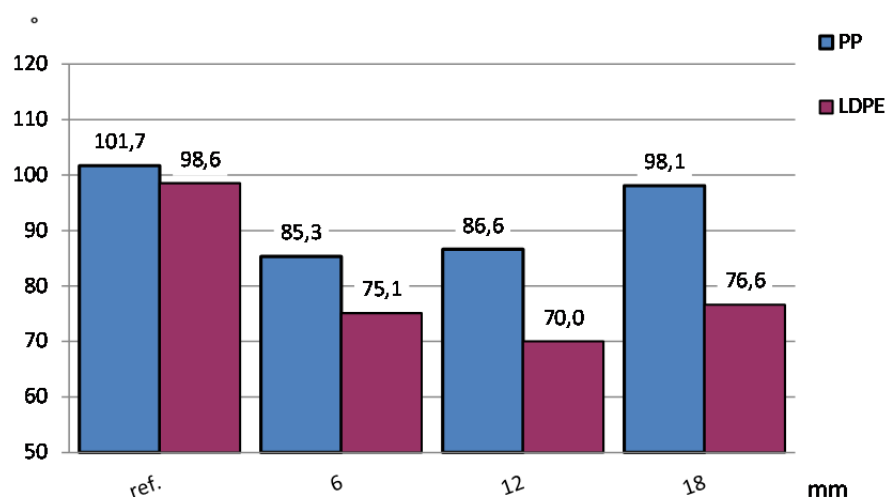


Figure 13. The influence of distance (mm) between the flame and the surface on CAW(°).

The air flow (Figure 15) had less effect on PP, compared to reference value. Both polymers had linear decrease in the contact angles when the air flow was on higher level. LDPE on the other hand, reacted strongly to gas flow changes compared to PP. Overall, PP's surface energy remained closer to the reference value.

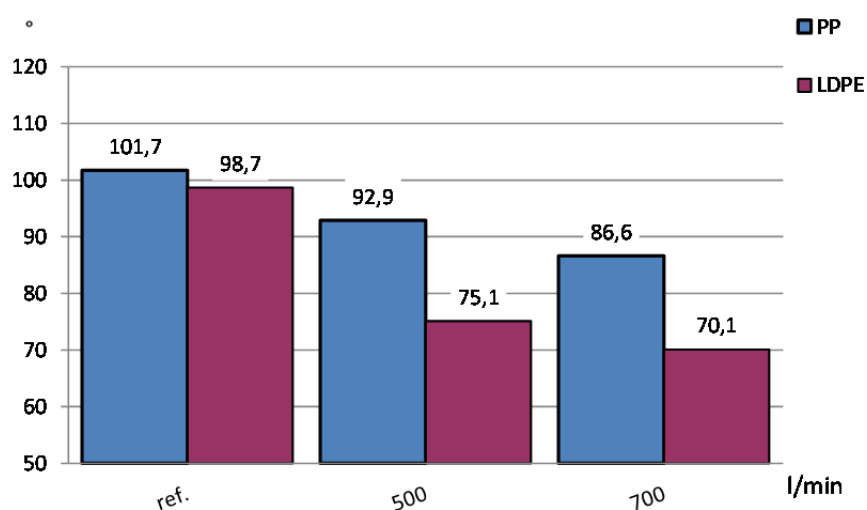


Figure 14. The influence of the flame treatment's air flow (l/min) on the surface's CAW (°).

WVTR

In flame treatment's effect on water vapour transmission rate, four aspects were investigated: track speed, air-gas ratio, distance between the track and the flame air flow.

In the study of process speed (Figure 16), PP had lower water vapour values in every study point and the difference to the reference value was greater than on LDPE. The changes in LDPE's values were imperceptible and no greater variation was discovered. PP's water vapour transfer resistance decreased linearly with the growth of process speed.

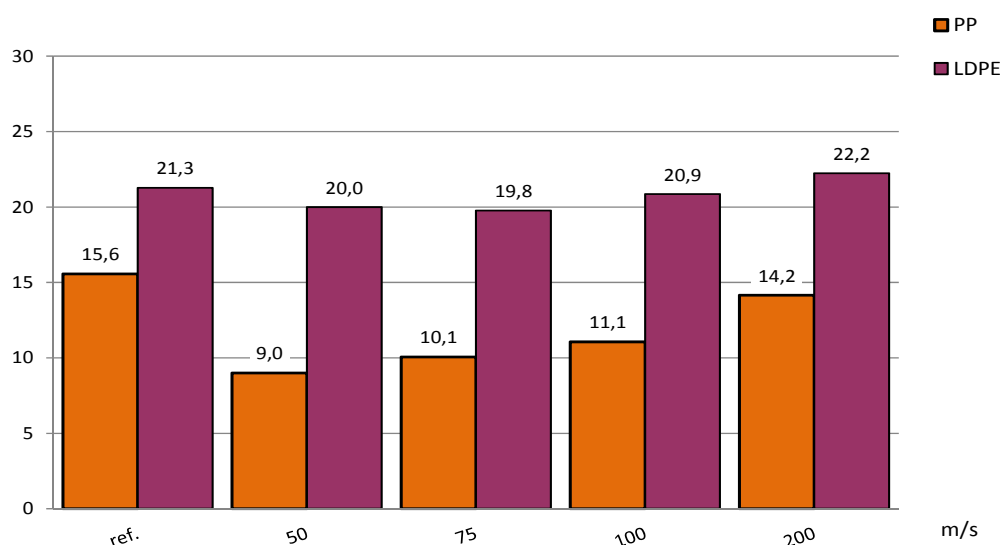


Figure 15. The influence of flame treatment's speed on WVTR (g/m^2).

All the studied air-gas ratios (Figure 17) gave relatively similar variation both PP and LDPE as the changes were inside possible error margin. LDPE gained the lowest water vapour intake in air-gas ratio 28:1. PP had lower water vapour transmission compared to LDPE in every study point. LDPE's values remained close to the reference point, when flame treatment seemed to enhance PP's barrier properties in every air-gas ratio.

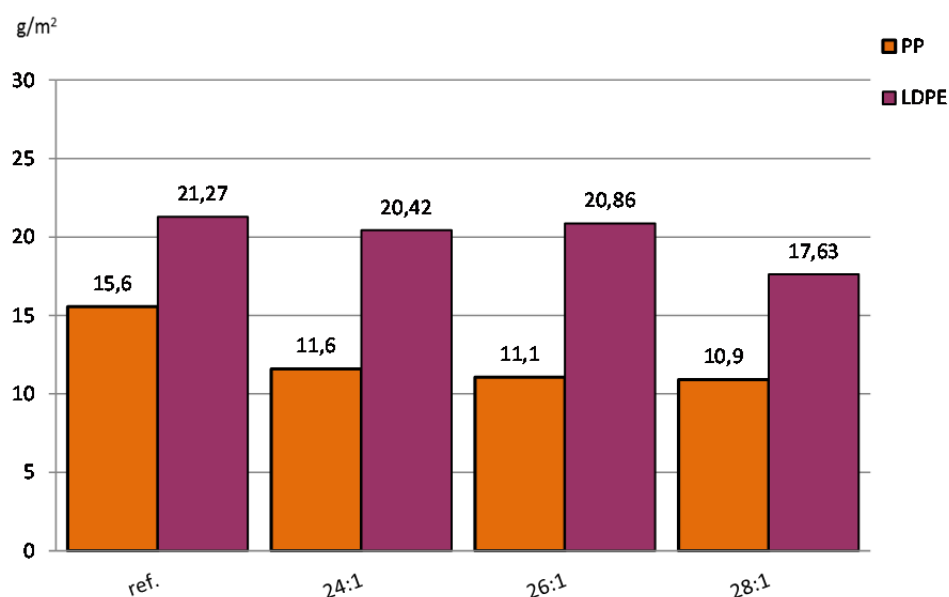


Figure 16. The influence of flame treatment's air-gas ratio on WVTR (g/m^2).

The distance of flame (Figure 18) did not have fair effect on LDPE's WVTR results. On PP, the results decreased when the distance grew in the first two study points. Also the difference between the reference point and these first two points were greater than on the LDPE. Apparently, there was something wrong in the test point where the distance between the track and flame was 18 mm: it is rather unlikely that water vapour intake could be on higher level than in the reference point. All the other test points seem to have better barrier compared to reference point.

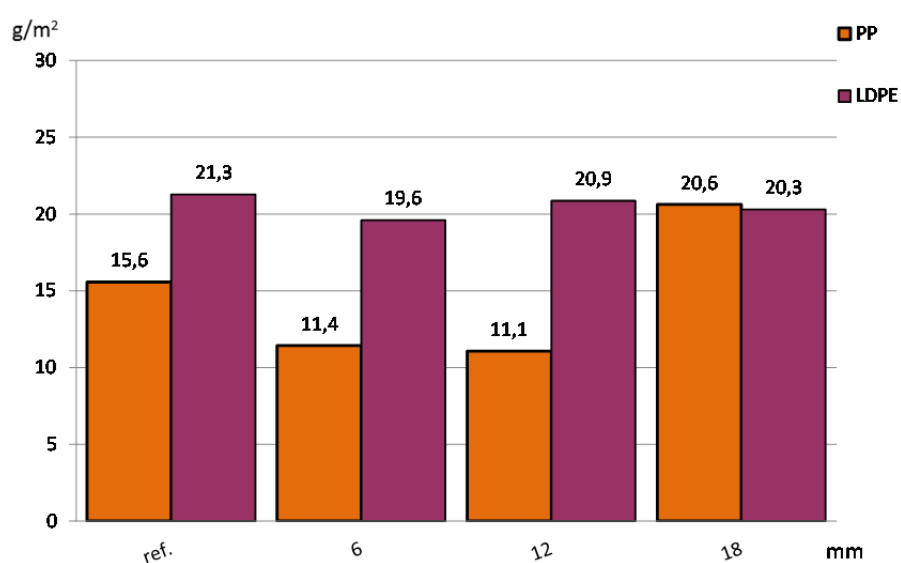


Figure 17. The influence of flame treatment's distance on WVTR (g/m^2).

The increase of air flow (Figure 19) seemed to enhance PP's barrier, when LDPE's results remained close to the reference values. PP seems to be sensitive on changes in parameters.

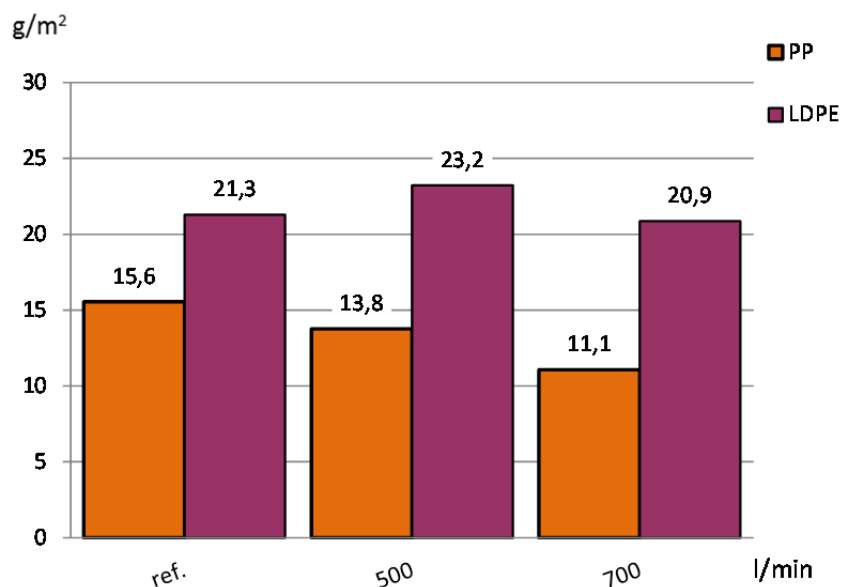


Figure 18. The influence of the flams treatment's air flow on WVTR (g/m²).

IST

To measure the lowest sealing temperature in various study points, the results have been organized as the effect of line speed, air-gas ratio, distance, air flow. The measuring data can no longer be found, and as the measurements were performed and analysed manually, the results are not as accurate as they should be.

In the reference point, PP had higher sealing temperature than LDPE (Figure 20), which can be explained by crystallization. Flame treatment raises the sealing temperature for both polymer grades. In spite of LDPE lower reference point value; this polymer has similar sealing temperature to PP, when the only changing parameter is the line speed (Figure 20). Also, it seems line speed had no impact on sealing temperatures as they remained relatively stable (150-170 C).

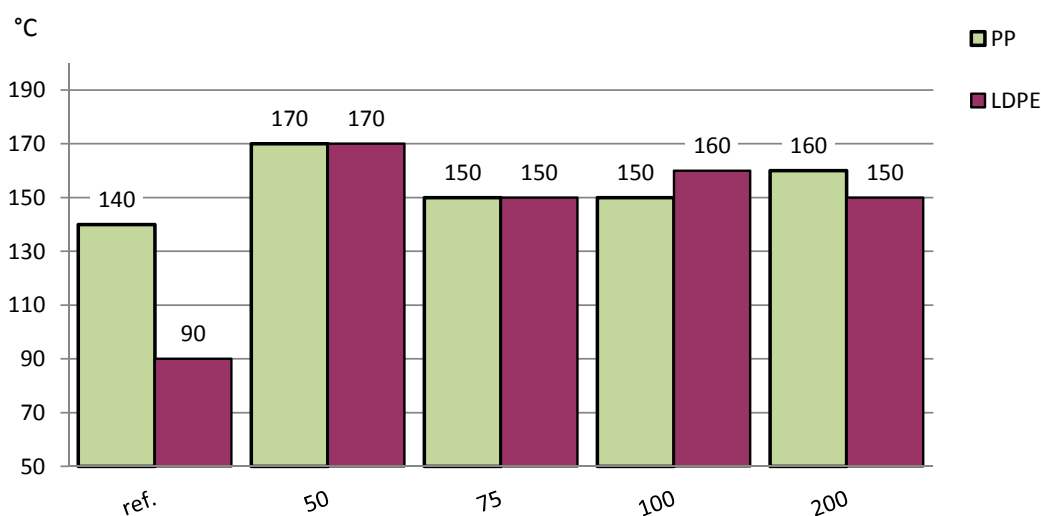


Figure 19. *The influence of the flame treatment's speed on IST.*

For both polymers the growth of air-gas ratio (Figure 21) lowered sealing temperature. However, LDPE had higher sealing temperatures in 50 % and 70 % air-gas ratio; but finally, in 100 % it had lower value than PP.

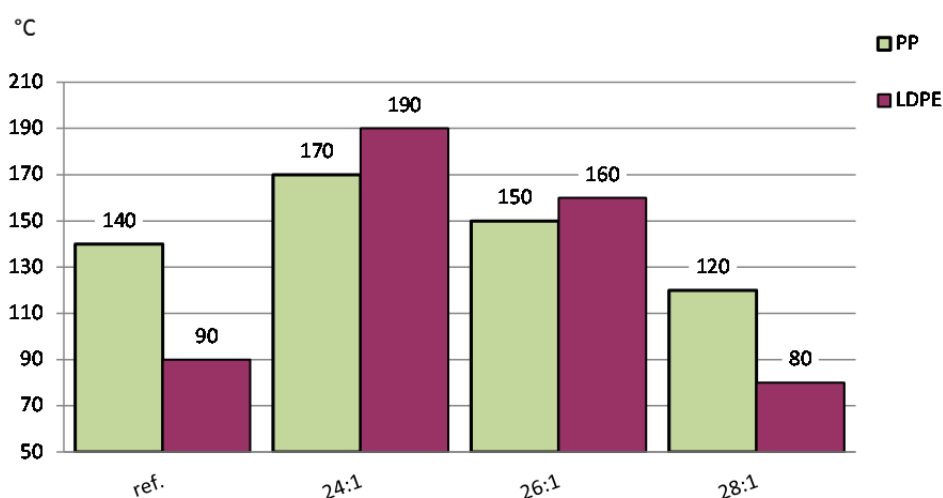


Figure 20. *The influence of the flame treatment's air-gas ratio on IST.*

The distance (Figure 22.) between surface and flame gained variable results. In 6 mm PP has similar sealing temperature that in the reference point and it slightly grows in larger distances. LDPE has dissenting result in 12 mm as it peaked in 160 °C, but in 6 mm and 12 mm it has lower sealing temperature. This is also the only value in distance variables where LPDE has greater value than PP.

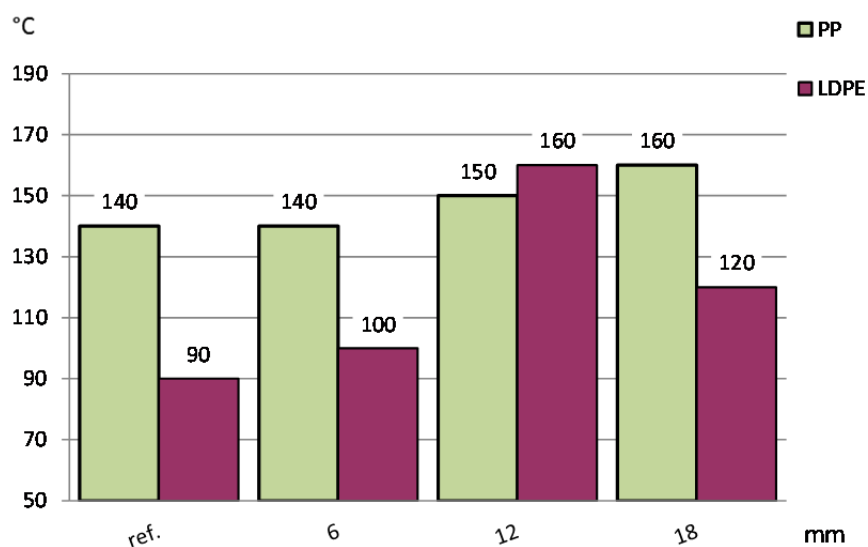


Figure 21. *The influence of the flame treatment's distance on IST.*

Air flow (Figure 23.) seem to grow LDPE's sealing temperature mostly in 700 m³/s air flow, while PP has relatively stable values close to reference temperature. Strangely, LDPE's sealing temperature was higher than PP in greater airflow, although PP's values were higher in reference point and in 500 m³/s air flow.

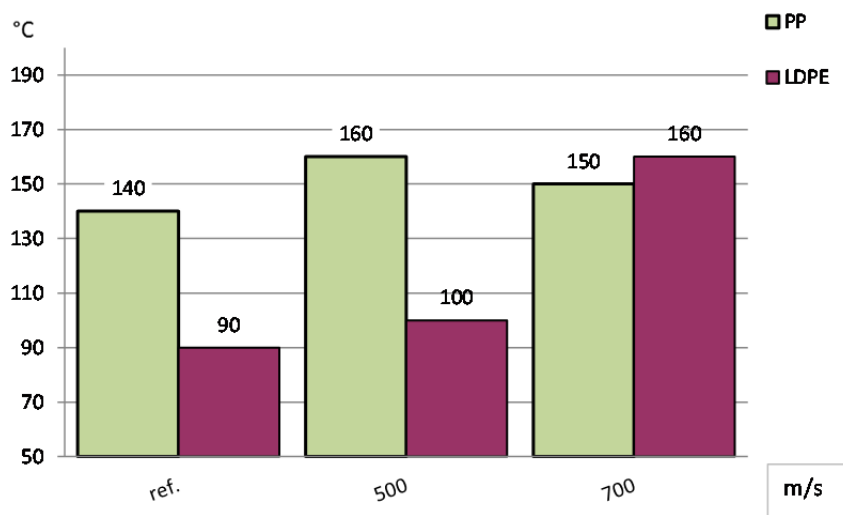


Figure 22. *The influence of the flame treatment's air flow on IST.*

The results may have been effected by the problems with Teflon jaws, but as the situation was the same in every study point, the results are tolerable.

5.2. The barrier effect (water) of flame, corona and atmospheric plasma treatment (Case 2)

Corona and plasma treatments were tested in comparison to flame treatment (Appendices 5. and 6.). The used parameters were the following:

- Flame
 - 50 m/min
 - 75 m/min
 - 100 m/min
 - 200 m/min
- Corona
 - 25 m/min (240 Wmin/m²)
 - 50 m/min (120 Wmin/m²)
- Plasma
 - 100 m/min (60 Wmin/m²)
 - 100 m/min (30 Wmin/m²)

In flame treatment (Figure 16.) LDPE had best WVTR result 17,63 g/m² in air-gas ratio of 28:1 while other parameters remained standard. In corona treatment flame the best WVTR result 18,36 g/m² was performed by 60 W power while line speed was 100 m/min, relatively similar result was performed by 300 W on line speed of 25 m/min. Plasma treatment with helium gas (Figure 24) gave result of 19,90 g/24h. Therefore best barrier didn't vary particularly on different treatments for LDPE.

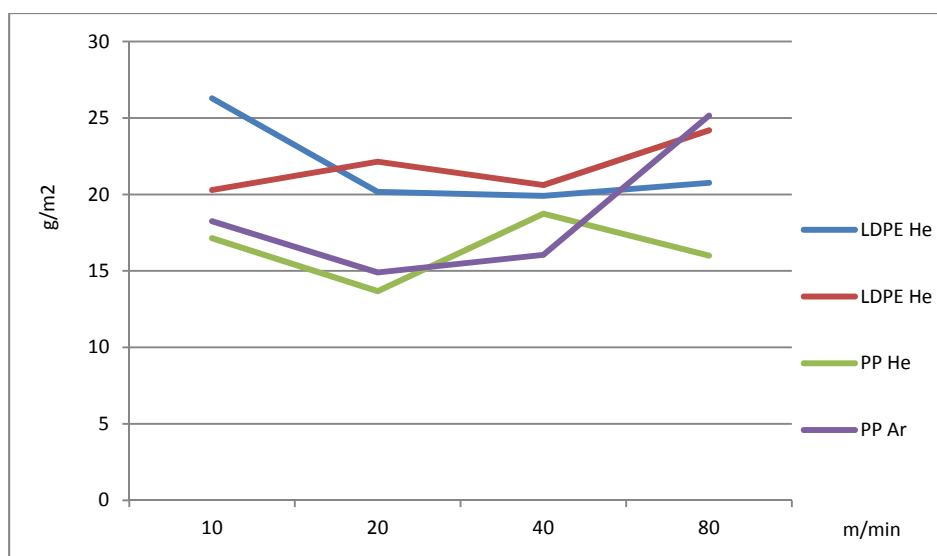


Figure 23. The effect of track speed on plasma treatment.

PP had its best barrier on slow line speed (75m/min) flame treatment: WVTR 10,07 g/m^3 . The result would probably been better on line speed 50 m/s, but unfortunately there were some problems with the sample: sealed edges leaked, thus result was not valid. As downside, slow line speeds on flame treatment caused low optical quality. Corona treatment didn't enhance PP's barrier: The best result for this treatment was 14,41 g/m^3 on 3000 W at 50 m/min line speed. Plasma results (Figure 24.) were quite similar to corona, best result being 13,68 g/m^3 on He-plasma at 20 m/min speed. Flame treatment reached better values nearly every test point compared to plasma and corona.

5.3. The effect of treatment combination (Case 3)

This test run was special as there is no known research on how the order of different treatments effect on the surface properties. The flame treatment was performed in every study point and two different air-gas rations were in use (1:24 and 1:28). The other investigated treatments were He- and Ar-plasma and corona. Both LDPE and PP were under the study. The used study point parameters were held similar for both air-gas ratio and polymers i.e. study gave four different results from same point. To find out the changes between treatments combinations (Appendices 7. and 8.), the used parameters were the following:

- Fl₁: 100 m/min, 12 mm, 24:1, 700 l/min
- Fl₂: 100 m/min, 12 mm, 28:1, 700 l/min
- He-plasma: 2000W/980W, 28.4 kHz, 2.3 A, 90 l/min
- Ar-plasma: 1800W/850W, 28.7 kHz, 2.1 A, 30 l/min
- Corona₁: 3000 W, 100 m/min
- Corona₂: 1500 W, 100 m/min

IST

In LDPE's treatments it seemed lower sealing temperatures occurred on higher rate of gas on the flame (Figure 25). None of the study points exceeded the temperatures 24:1 gas ratio study points gave. The lowest sealing temperature in 24:1 gas ratio was in the point where the flame treatment was performed before corona. The other study point in this study point had more than 40 C higher temperatures. The greatest temperature difference between used air-gas rations were performed on flame-Helium plasma treatment. For both gas ratio studies the highest temperature was discovered in a point where He-has plasma treatment took place before the flame treatment.

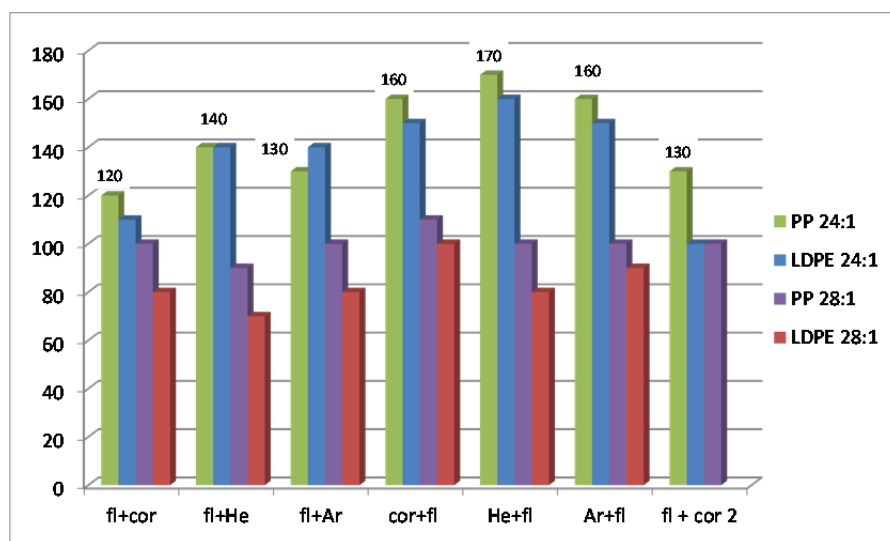


Figure 24. The influence of the treatment order on IST (°).

PP's results followed similar curve as LDPE: angles were smaller on 24:1 gas ratio and the study points where flame treatment was performed first, reached lower sealing temperatures. The sealing temperatures were highest on He-plasma-flame treatment; lowest point for 24:1 was on flame-corona treatment and in 28:1 flame-helium plasma treatment.

CAW

For LDPE it seemed that lower contact angles were achieved when the flame treatment was first (Figure 26). In gas ratio 24:1 angles were slightly larger, but the results followed the angles from higher gas ration's study points. No great differences were discovered between corona-, Ar- and He-plasma results, when these treatments were performed after the flame. All of these treatments gave high contact angles. In lower gas ratio the lowest contact angle was in the study point where Ar-gas plasma treatment was performed after the flame. In Higher gas rate the highest surface energy was produce by treatment order flame + corona. Greatest gap between two different gas ratios were discovered on flame-corona treatment.

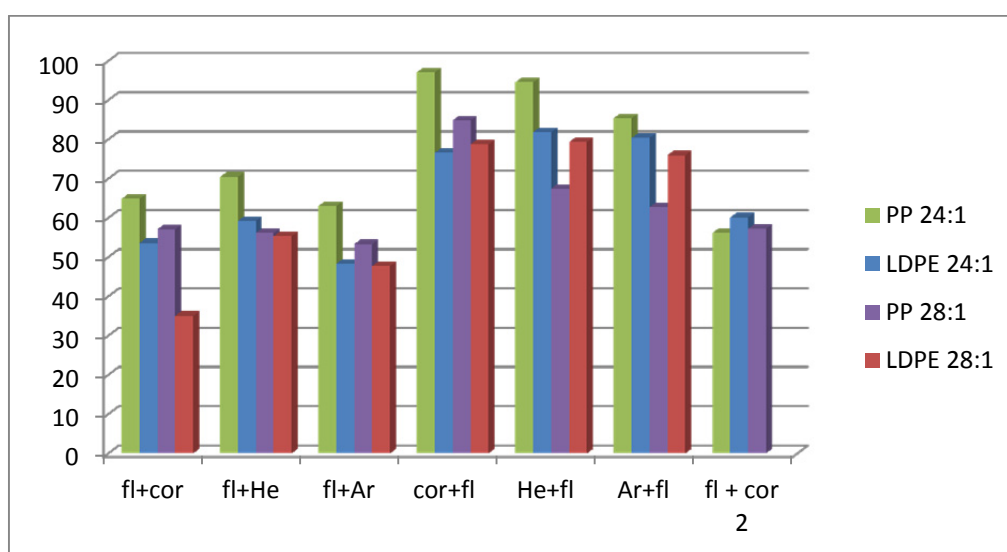


Figure 25. LDPE's and PP's contact angles (°) in various treatment orders on different air-gas ratios.

PP's contact angles were larger in air-gas ratio 24:1, except when the corona treatment was stronger. On 28:1 the results were closer or even under of LDPE's corresponding values than on the other gas rate. As a similarity to LDPE, PP's contact angles were smaller on study points where the flame treatment was first in the order.

WVTR

The higher air-gas ratio (Figure 27.) lowered flame-corona treatment's WVTR results, other remained relatively similar as on lower (1:24) gas ratio. In lower gas ratio the variation of the barrier properties was quite low, when on the higher gas ratio, there were significant differences between the study points. There may have been some errors in WVTR measuring.

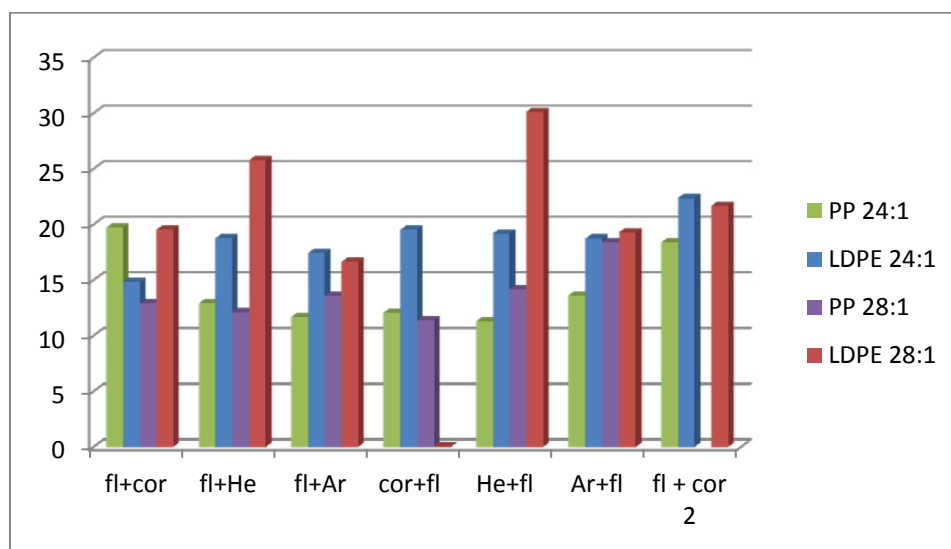


Figure 26. *The influence of the treatment combination on WVTR (g/m³).*

In the lower gas ratio the lowest WVTR results occurred on flame-plasma treatments, other values remained quite close to each other. In 28:1 gas ratio lowest WVTR value took place in a study point where corona treatment was performed before the flame. This barrier result was excellent in comparison of the other study points. The largest difference between similar study points, in studied gas ratios, occurred in treatment of He-plasma and flame, gaining one third more water inside the sample cup than on the higher gas rate.

5.4. The Influence of Time and Conditions (Case 4)

The influence of time and conditions was measured by CAW, IST and hot tack. The following treatments were investigated:

- Helium-plasma 10 m/min
- Helium-plasma 40 m/min
- Argon-plasma 10 m/min
- Argon-plasma 10 m/min
- Flame 1:24
- Flame 1:28
- Corona 25 m/min
- Corona 100 m/min

The used conditions were tropical (38 °C, RH 90 %), mild (25 °C, RH 75 %) and normal temperature (23°C, RH 50 %). CAW measurements were performed on test run day, 24 hours, 48 hours, one week and one month after the test run. CAW test were performed six month later, but the results got missing. IST test were performed in 24 h, two weeks, one month and 6 month after the test run. The detailed accurate results can be seen in Appendices 9, 10, 11 and 12.

CAW

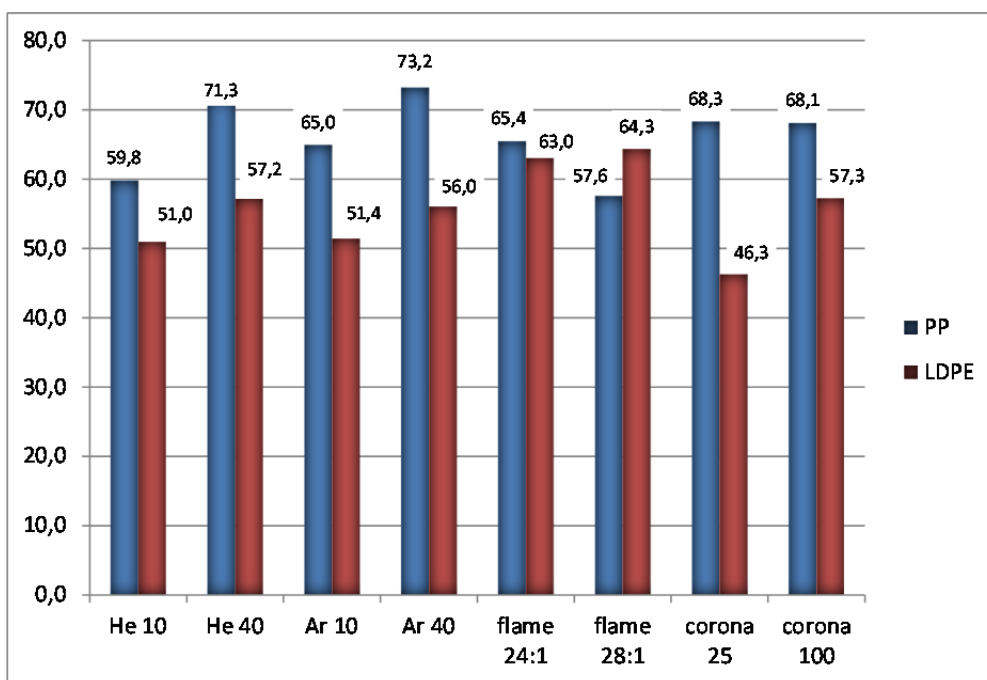


Figure 27. Contact angles(°) on reference values in time influence series.

On the test run day (Figure 28.) all the treatments gave lower contact angle values to LDPE, except the flame in 28:1 gas ratio. Largest gap between the tested polymers was in corona 25 treatment: PP had nearly 20 degrees larger contact angle than LDPE. Also, this study point showed the highest surface energy on LDPE. PP had its largest angle in Ar 40 plasma. Also He 40 gave relatively similar value. The smallest contact angle and highest surface energy for PP was discovered in flame 28:1, at the same time LDPE had its largest angle in the same study point.

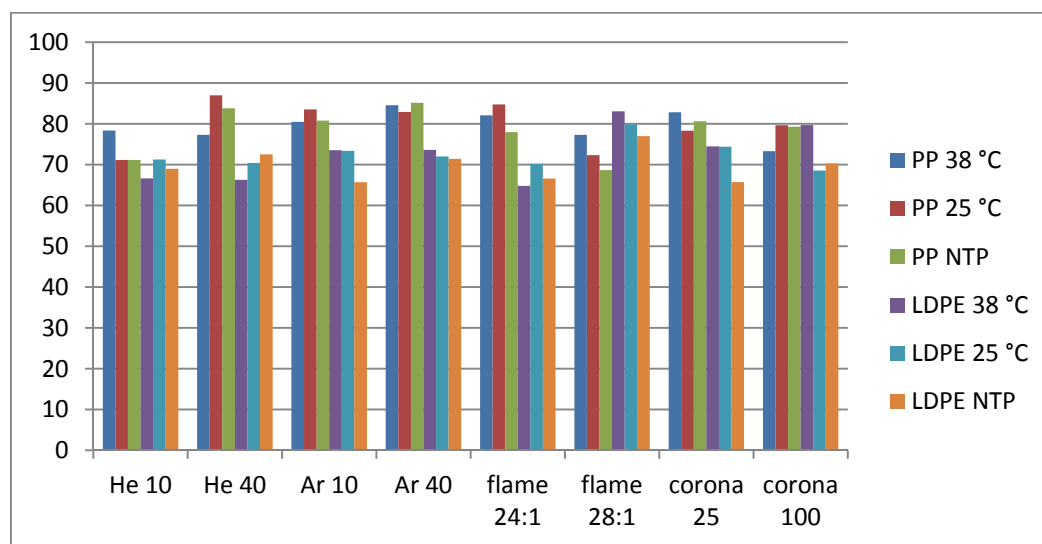


Figure 28. Contact angles (°) 24 h after the treatments.

In the first day after the test run (Figures 28 and 29), all the contact angles grew despite the polymer and the conditions, although the growth on PP compared to previous results was not as remarkable as on LDPE. LDPE also had more differences between the study points in different conditions: the higher the temperature, the greater contact angles. Highest peak for PP was achieved by He-40 in mild conditions; LDPE reached largest angles in flame 28:1 gas ratio in all conditions as it had reached in the first tests as well. Lowest surface energy was on LDPE in tropical conditions on flame 24:1. Also Helium plasmas gave low values in this condition. LDPE had small angles also in NTP conditions in Ar 10, flame 24:1 and corona 25.

48 hours after the treatments (Figure 30.) the growth of contact angles had decelerated and the values were relatively close to 24 h results. Again, the highest peak on PP appeared in 40 He-plasma treatment, but now in tropical conditions. Flame 28:1 in tropical conditions decreased the contact angle. As the measuring tool was not as reliable, these results might have some changes that are not valid. But what can be seen from the results, the differences between 24 h and 48 hour after the treatment were insignificant. The influence of different conditions was also shown as for LDPE, the contact angles grew when conditions were warmer. LDPE was more receptive on condition change than PP.

One month after the test run (Figure 30.), the results had not changed remarkably. Once again, the measuring tools might have affected on results, but the curve can show that despite few occasional changes, the general level of surface energy had remained the same as before. Two months after the treatment the growth on contact angles was greater in study points that had been kept in tropic conditions. Both LDPE and PP peaked in AR-plasma 40 in tropic conditions. In every measurement point both polymers got higher contact angles on samples that had been in warmer and humid conditions. The results followed logarithmic curve.

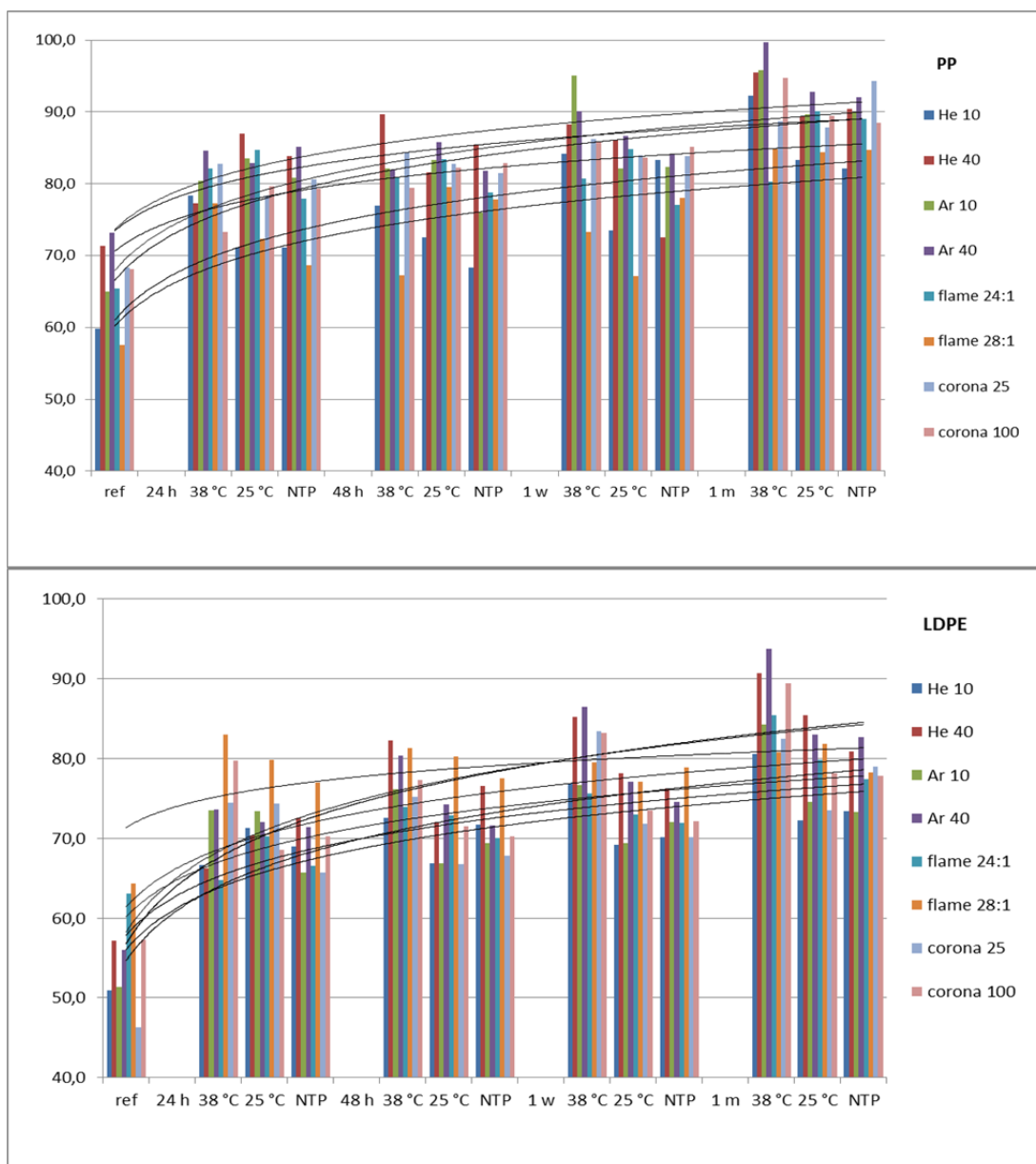


Figure 29. Contact angles (°) in function of time (logarithmic trend lines).

IST

The greatest change of the sealing temperature (Figure 31) took place on flame treatment in air-gas ratio 24:1. Also, the highest value for both studied polymers was in this particular study point. In LDPE, the contact angles kept reducing in the first month after the study, but in 6 months the result reached higher values than ever before. PP, on the other hand, had high sealing temperature in 24:1 to begin with, and its study point gave the lowest value after two weeks.

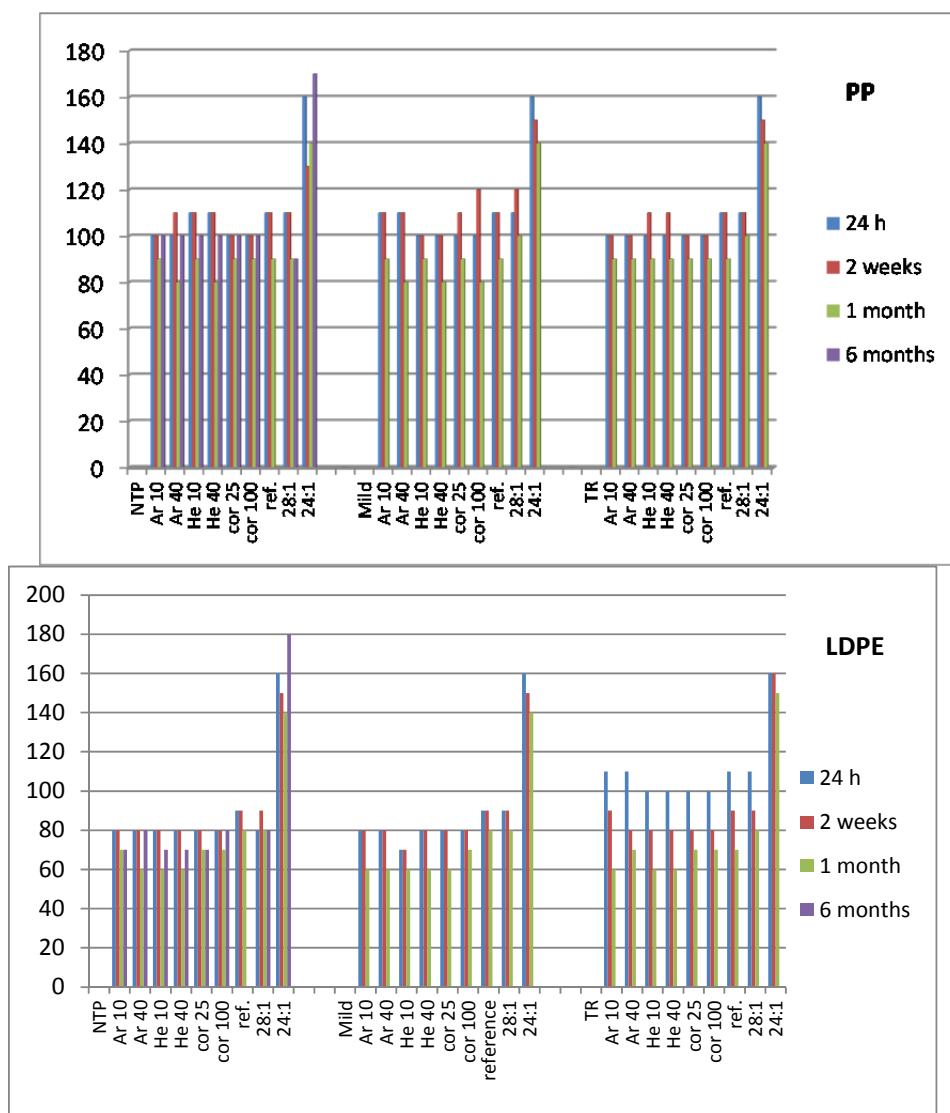


Figure 30 The influence of time and conditions on LDPE's sealing temperature (°C).

All the other treatments had relatively similar values throughout the measurements, and the variation of the result was low, however, in one month the contact angles reached the lowest values in the study points on both polymers. As this same phenomenon happened in reference point as well, it can be interpreted as a feature for polymers.

Hot Tack

The hot tack tests were performed in two phases: 24 hours and a month after the test run. The samples that were measured one month after the test run were kept in different conditions. The temperatures that produced highest hot tack strength were relatively similar (Figure 33) in both polymers on corresponding study points, except on reference values.

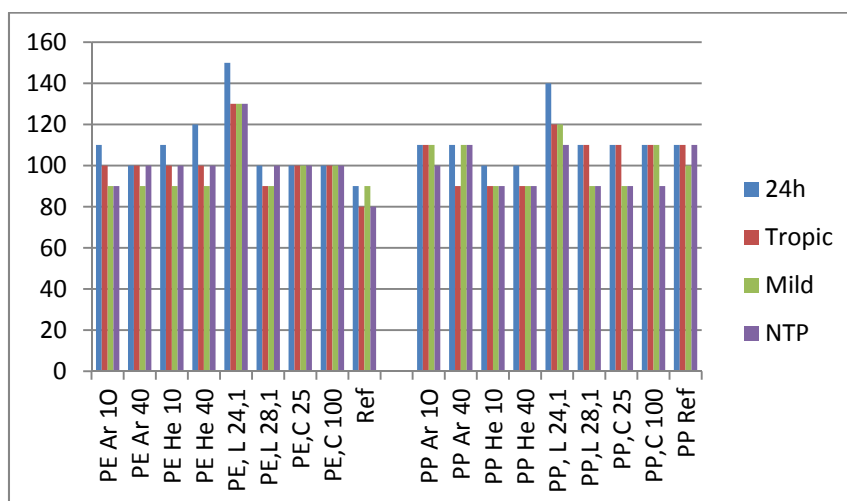


Figure 31. Hot tack temperatures (°) 24 h and one month after the test run in different conditions.

PP had lower hot tack temperature in helium-plasma in every condition one month after the test run. Also corona-treated study points received lower hot tack temperature on PP in mild and NTP conditions.

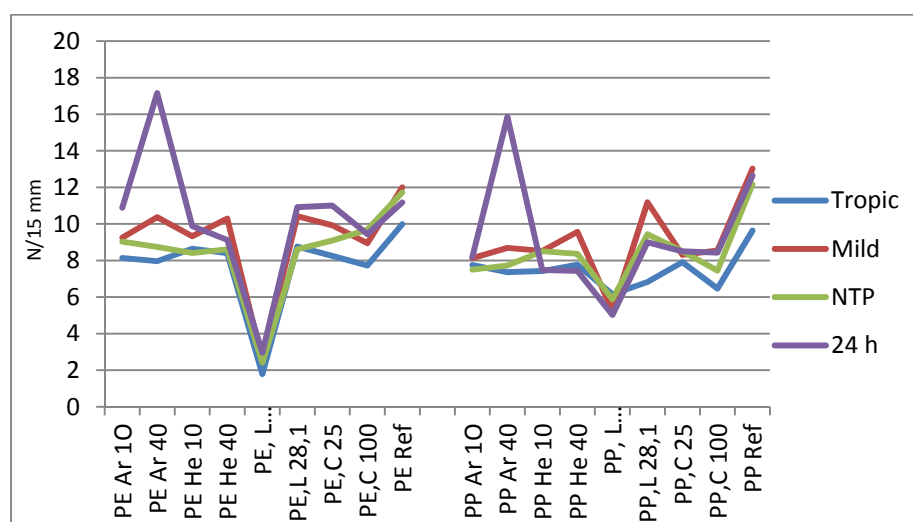


Figure 32. Hot tack forces in different conditions on variable treatments.

In the hot tack strengths (Figure 34), PP's values had less variation inside the study points. In hot tack runs both PP and LDPE reached lowest value in 24:1 air-gas ratio flame treated sample that had been kept in tropical conditions. Both polymers had distinguishable hot tack strength in argon-plasma treatment in speed of 40m/s in 24 hours after the treatment, but this strength had disappeared in one month in every conditions. LDPE's values had less variation between the study points. PP had lower values on plasma treatments and corona than LDPE, although its reference value was greater than LDPE's.

6. DISCUSSION

Case 1

It was proven that PP has better barrier features than LDPE, both on untreated and flame treated surfaces. PP's crystallized structure creates tight surface that has an excellent chemical resistance. When it comes to the changes of barrier features, PP reacts strongly to the flame treatment: greatest changes are discovered in the effect of the line speed and the gas flow. Relatively slow line speed and high air flow gives the best barrier, although extremely slow speed together high air flow may cause optical failure i. e. stripes. LDPE's barrier enhances on flame treatment as well, but the results are weaker than on PP and there is no great variation between different study points. The flame treatment melts polymer structure and molecules will re-organize in the surface and create higher crystallinity. As a result the structure will become stronger. Most likely PP's linear polymer structure is more receptive towards changes in crystallinity. In Mikko Tuominen et al. study indicated that the thermal effect of flame increased the crystallinity and cross linking on the top surface of LDPE. In the case of PP coating the crystallization took place in PE portion. [23] In a research of PLA's WVTR it was shown that crystallized areas grow in microscope picture where the polymer has been in suitable temperature for long enough. [25] It might be possible that the temperature during the flame treatment suits better on PP than to LDPE in terms of crystallization.

The greatest growth in surface energy was discovered on LDPE. This polymer was also more sensitive to the flame treatment in general and the changes in parameters gave differing results. Due to PP's structure, it has strong inner forces that resist surface energy. Flame treatment can reduce contact angles by changing surface's oxidization and chemical properties. As a result, the surface energy can be improved. In this trial PP's surface energy changes were slightly weaker in comparison to similar study points on LDPE, nevertheless the results were tolerable (in terms of technical use).

According to the performed studies, PP's sealability temperatures remained relatively constant in flame treatment despite the flame treatment parameters. The lowest sealing temperature was discovered on higher air-gas ratio on flame treatment. The sealing temperatures are relatively close to reference point and they do not particularly differ from LDPE's values when the only changing parameter is the line speed. LDPE's has lower sealing temperature on untreated surface and it tends to grow by flame treatment, although with correct parameters the sealing temperature can be relatively low. In conclusion, flame treatment has less effect on PP, but as the sealing

temperatures are high in every study point, PP sets challenges to polymer products that require heat-seal.

Case 2

As a comparison for flame treatment results, some study points of corona and plasma treatments were investigated. Best barrier results for LDPE were achieved in the flame treatment with air-gas ratio 28:1. From compared treatments the best result was performed by corona in 300W, plasma gained slightly better results than the other flame parameters. In conclusion, LDPE's barrier remained fairly similar in all treatments. Lack of optical properties in higher gas-ratio flame treatment would prevent its industrial use, although it gave the best barrier results. Therefore for LDPE, the best treatments are corona and plasma when focusing on barrier properties.

PP reached its best barrier properties in flame treatment when the line speed was very low. Slow line speed is not particularly economical and also the optical properties will sustain when the flame is directed to the polymer surface for longer time. Unlike LDPE, PP's barrier properties did not improve on corona or plasma. The best treatment for PP in terms of barrier properties is flame treatment with reasonable line speed and distance from the track, high air-gas ratio and air flow. Unfortunately slow line speed, small distance between the flame and the track and high air flow may cause stripes and other optical harms that are unflattering for the product. J. Park et. al. explained the uniformity in PP's flame treated surface is caused by a variation in the surface energy. [26]

Case 3

In the study of treatment order, it seemed the best surface energy was achieved when the flame treatment was performed before corona or plasma for both studied polymers, although LDPE kept having smaller contact angles in comparison to the similar PP study points. The highest surface energy was discovered on LDPE when the flame treatment had higher air-gas ratio and when there was corona treatment performed afterwards. On PP the smallest contact angles were in treatment pair flame 28:1 and argon-plasma. J. Lahti et al. study referred that flame treatment decreased the contact angle on water on LDPE and PP coated papers more than corona, but the lowest angles were obtained when treatments were used simultaneously. [24] Therefore, this conclusion was confirmed in this study. In Heikki Lappalainen's master's thesis it was also shown LDPE and PP grow most surface energy on combined flame and corona treatment. LDPE receive lower contact angles on corona treatment in comparison to flame and PP has better surface energy on flame treatment. [16]

LDPE and PP followed similar curve in sealing temperatures, although the air-gas ratio gave higher sealing temperatures for both polymers. LDPE's results were slightly above PP's values in every study point. Lowest sealing temperatures took place in

treatment combination where flame treatment was first in the order. It seemed the order of treatment did not have strong effect on WVTR results.

Apparently, the flame treatment prepares the surface for other treatments. As the flame treatment changes the surface's oxidization, the other treatments can enhance surface's other chemical properties. For instance, plasma treatment breaks molecular bonds exposing new sites for other chemical bonds. As a result the surface energy grows and sealing temperatures reduce. Flame and corona treatments increase the surface energy by introducing oxygen containing functional groups on the surfaces of LDPE and PP. [24] Together these treatments reach better values than alone, but if flame treatment is performed after corona or plasma treatment, the flame treatment prevent their impact. In Farley et. al. studies it was proofed that any level of corona treatment is sufficient to change the failure of heat seals prepared from LLDPE and the increase in seal initiation temperature is 5-17 °C [10]. Either LLDPE differ from LDPE and PP, or this phenomenon did not occur when there were two different treatments used. J. Lahti et. al. on the other hand, referred that the flame treatment deteriorates the sealability properties on LDPE, whereas corona treatment improves sealability by decreasing the minimum heat sealing temperature. In this point of view, the studied result endorses this conclusion.

Case 4

In the study of time and conditions, the contact angles grew in logarithmic scale on every studied treatment on both polymers. The results varied inside the study points and as measuring tools were not as reliable as required, no excessive conclusion can be drawn on one certain study point. The fastest decrease in the surface energy took place within the first 24 hours after the treatment. It was also shown that humidity and higher temperature had significant effect on contact angles growth.

Heat sealing temperature remained relatively similar in every condition and some changes can be explained by measuring errors. Also, in most study points the sealing temperatures reached their highest values in 24 hours. On LPDE the most remarkable changes happened in tropical conditions as the highest values turned lowest in 6 month time. PP's values had less variation inside the study points.

In R. H. Cramm's study it was mentioned that the lower surface tension facilitates sealing at lower temperature. [28] PP had lower hot tack temperature in helium-plasma in every condition one month after the test run. Also corona-treated study points received lower hot tack temperature on PP in mild and NTP conditions. The result has conflict with the contact angel measurements as the surface energy lowered in time. In hot tack force measurements both PP and LDPE reached lowest value in 24:1 air-gas ratio flame-treated sample that had been kept in tropical conditions. Most PP samples had fibre tearing in hot tack measuring, which means the actual hot tack strength was not measured as extruded polymer took off from the substance. Also, in the hot tack

strengths PP's values had less variation inside the study points. The reason why both polymers had distinguishable hot tack strength in argon-plasma treatment in speed of 40 m/s in 24 hours after the treatment was probably because the surface tension was on low level or the treatment had changed the chemical properties unusual way in this study point. PP had lower values on plasma treatments and corona than LDPE, although its reference value was greater than LDPE's, therefore there is a great potential to develop PP's use in packaging industry.

7. CONCLUSIONS

The performed case studies gave wide perspective on LDPE's and PP's properties and on the effects of different surface treatments. In the results, it was confirmed that PP has better water vapour transfer resistance throughout the study points and in comparison to LDPE it also reacted more on the surface treatments in case of WVTR. LDPE has higher surface energy in nearly every study point despite the surface treatment and its reaction on treatments was greater than what PP has. The best surface energy for both polymers would be achieved by lower air-gas ratio, slower track speed, relatively high air flow and small treatment distance. LDPE's and PP's heat sealability temperatures are relatively close to each other in treated study points, though LDPE's reference value is remarkably lower.

If flame treatment is combined with plasma or corona, the best results for both used polymers will be achieved when the treatment order where the flame treatment is performed first: sealing temperature, surface energy and WVTR all will enhance. In the study of time condition contact angles grow in logarithmic scale in both studied polymers and the highest growth happens in warmer and humid conditions. Therefore, all the treatments lose their effect mainly within first 24 hours after the treatment. LDPE's and PP's sealing temperatures follow relatively similar curve in function of time. PP can have better hot tack values than LDPE when used corona and plasma treatment. As hot tack-properties defines how the package can cope the packaging process without breaking in the manufacturing line, this could be a possibility to gain more popularity for PP.

These two studied polymers have relatively similar properties, considering they have such a differing polymer structure. PP do have some challenges in terms of processability, but with suitable parameters it can be widely used in extrusion coating, especially in the products that require better barrier properties, and good printability is not as essential.

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APPENDICES

Nopetus										
linja/kaasu	26:1									
etäisyys	12									
virtaus	700									
Nopetus	ref.	50	75	100	200					
I.S.T	140	170	150	150	160					
CAW	101,8	86,7	88,8	86,6	95,2					
WTR	15,56	10,07	11,07	14,16	14,16					
GSM	17,51	18,24	19,22	19,99	19,82					

linja/kaasu

nopetus	100
etäisyys	12
virtaus	700
linja/kaasu	ref.
I.S.T	140
CAW	101,8
WTR	15,56
GSM	17,51

Etäisyys

nopetus	100
linja/kaasu	26:1
virtaus	700
Etäisyys	ref.
I.S.T	140
CAW	101,8
WTR	15,56
GSM	17,51

Virtaus

nopetus	100
linja/kaasu	26:1
etäisyys	12
Virtaus	ref.
I.S.T	140
CAW	101,8
WTR	15,56
GSM	17,51

CAW/ Etäisyys

linja/kaasu	26:1
etäisyys	12
virtaus	700
Nopetus	ref.
CAW	106,0
	84,2
	86,4
	87,5
	86,9
	84,9
	99,0
	102,4
	100,2
	101,8
keskiarvo	101,8

CAW/ linja/kaasu

nopetus	100
etäisyys	12
virtaus	700
linja/kaasu	ref.
	106,0
	101,0
	102,9
	100,8
	99,0
	102,4
	100,2
	101,8
keskiarvo	101,8

WTR/ Etäisyys

linja/kaasu	26:1
etäisyys	12
virtaus	700
Nopetus	ref.
WTR	14,332
	16,204
	16,148
	15,56
keskiarvo	15,56
hajonta	1,07

WTR/ linja/kaasu

nopetus	100
etäisyys	12
virtaus	700
linja/kaasu	ref.
WTR	14,332
	16,204
	16,148
	15,56
keskiarvo	15,56
hajonta	1,07

WTR/ Etäisyys

nopetus	100
linja/kaasu	26:1
virtaus	700
Etäisyys	ref.
WTR	14,332
	16,204
	16,148
	15,56
keskiarvo	15,56
hajonta	1,07

CAW/ virtaus

nopetus	100
linja/kaasu	26:1
etäisyys	12
Virtaus	ref.
WTR	14,332
	16,204
	16,148
	15,56
keskiarvo	15,56
hajonta	1,07

GSM/ Nopetus

linja/kaasu	26:1
etäisyys	12
virtaus	700
Nopetus	ref.
	16,35
	18,35
	17,78
	17,28
	17,78
	17,28
	17,51
keskiarvo	17,51
hajonta	0,64

GSM/ linja/kaasu

nopetus	100
etäisyys	12
virtaus	700
linja/kaasu	ref.
	16,35
	18,35
	17,78
	17,28
	17,78
	17,28
	17,51
keskiarvo	17,51
hajonta	0,64

GSM/ Etäisyys

nopetus	100
linja/kaasu	26:1
virtaus	700
Etäisyys	ref.
	16,35
	18,35
	17,78
	17,28
	17,78
	17,28
	17,51
keskiarvo	17,51
hajonta	0,64

GSM/ virtaus

nopetus	100
linja/kaasu	26:1
etäisyys	12
Virtaus	ref.
	16,35
	18,35
	17,78
	17,28
	17,78
	17,28
	18,15
keskiarvo	18,15
hajonta	0,64

Appendix 2. LDPE flame WVTR

Energia- ja prosessiteknikan laitos
Paperinjalostus- ja pakkaustekniikka



TAMPEREEN TEKNILLINEN YLIOPISTO

Vesihöyrynläpäisevyys ASTM E96										
Työn tilaaja:		Mikko Tuominen								
Projektitunnus:		WVTR LDPE								
Näytteet/koeajo:										
Standardi/menetelmä:		Lämpötila (°C): 38 Suhteellinen kosteus (% RH): 90								
Laboratorion työnumero:										
Työn suorittaja / valmis:										
Tulokset:										
	Pvm	15.12	16.12	17.12.200	18.12					
	Klo	14.20	14.40	14.15	13.40					
	kp 7-1	63,2868	63,3783	63,4800	63,5833	Erotus 1	Erotus 2	Erotus 3		
	kp 7-2	64,6039	64,6959	64,7828	64,8706	0,0915	0,1017	0,1033		
	kp 7-3	67,6272	67,7220	67,8124	67,9035	0,092	0,0869	0,0878		
	kp 7-4	65,4217	65,5672	65,6924	65,8073	0,0948	0,0904	0,0911		
	kp 7-5	65,3455	65,4388	65,5283	65,6198	0,1455	0,1252	0,1149		
						0,09332	0,0895	0,0915		
						KA	0,10342	0,09874	0,09772	
						WVTR g/m²	20,6848	19,748	19,544	19,9923
	Pvm	15.12	16.12	17.12.200	18.12					
	Klo	14.23	14.44	14.15	13.45					
	kp 8	67,6243	67,7075	67,7869	67,8665	Erotus 1	Erotus 2	Erotus 3		
		67,0568	67,2291	67,3793	67,524	0,0832	0,0794	0,0796		
		66,6445	66,7584	66,8543	66,9429	0,1723	0,1502	0,1447		
		75,9266	76,0120	76,0911	76,1717	0,1139	0,0959	0,0886		
		75,0698	75,1483	75,2233	75,2987	0,0854	0,0791	0,0806		
						0,0785	0,075	0,0754		
						KA	0,10666	0,09592	0,09378	
						WVTR g/m²	21,332	19,184	18,756	19,753
	Pvm	15.12	16.12	17.12.200	18.12					
	Klo	14.26	14.47	14.19	14.47					
	kp 9	83,1013	83,1943	83,2813	83,3679	Erotus 1	Erotus 2	Erotus 3		
		79,3829	79,4803	79,5691	79,6588	0,093	0,087	0,0866		
		78,1171	78,2052	78,2898	78,3759	0,0974	0,0888	0,0897		
		59,5858	59,6745	59,7608	59,8476	0,0881	0,0846	0,0861		
		60,1507	60,2392	60,3227	60,4097	0,0887	0,0863	0,0868		
						0,0885	0,0835	0,087		
						KA	0,09114	0,08604	0,08724	
						WVTR g/m²	18,228	17,208	17,448	
	Pvm	15.12	16.12	17.12.200	18.12					
	Klo	14.29	14.52	14.23	14.50					
	kp 10	75,8539	75,9626	76,0665	76,1701	Erotus 1	Erotus 2	Erotus 3		
		82,3401	82,4444	82,5454	82,6471	0,1087	0,1039	0,1036		
		80,0819	80,1841	80,2821	80,3821	0,1043	0,101	0,1017		
		79,3633	79,4698	79,5689	79,6689	0,1022	0,098	0,1		
		63,2248	63,3255	63,4213	63,5173	0,1065	0,0991	0,1		
						0,1007	0,0958	0,096		
						KA	0,10448	0,09956	0,10026	
						WVTR g/m²	20,896	19,912	20,052	
	Pvm	15.12	16.12	17.12.200	18.12					
	Klo	14.32	14.54	14.26	13.52					
	kp 11	56,8959	56,9052	56,9208	56,9171	Erotus 1	Erotus 2	Erotus 3		
		45,5578	45,5729	45,5804	45,5842	0,0093	0,0156	-0,0037		
		55,7724	55,7841	55,7912	55,7947	0,0151	0,0075	0,0038		
		57,8734	57,8856	57,8934	57,8999	0,0117	0,0071	0,0035		
		56,9112	56,9235	56,9314	56,9351	0,0122	0,0078	0,0065		
						0,0123	0,0079	0,0037		
						KA	0,01212	0,00918	0,00276	
						WVTR g/m²	2,424	1,836	0,552	
	Pvm	15.12	16.12	17.12.200	18.12					
	Klo	14.35	14.57	14.28	13.55					
	kp 12	69,2529	69,3751	69,4895	69,6019	Erotus 1	Erotus 2	Erotus 3		
		73,9003	74,0342	74,1543	74,2697	0,1222	0,1144	0,1124		
		84,2152	84,3167	84,4134	84,5132	0,1339	0,1201	0,1154		
		72,9495	73,0477	73,1409	73,2328	0,1015	0,0967	0,0998		
		63,3921	63,4893	63,5818	63,6738	0,0982	0,0932	0,0919		
						0,0972	0,0925	0,092		
						KA	0,1106	0,10338	0,1023	
						WVTR g/m²	22,12	20,676	20,46	
	Pvm	15.12	16.12	17.12.200	18.12					
	Klo	14.38	15.00	14.31	13.57					
	kp 13	65,04	65,1404	65,2357	65,333	Erotus 1	Erotus 2	Erotus 3		
		69,0909	69,1929	69,2883	69,3835	0,1004	0,0953	0,0973		
		70,8186	70,9212	71,0177	71,1145	0,102	0,0954	0,0952		
		68,6706	68,7737	68,8708	68,9669	0,1026	0,0965	0,1368		
		65,6778	65,7778	65,8778	65,9778	0,1031	0,0971	0,0961		
						0,2165	0,1952	0,1875		
						KA	0,12492	0,1159	0,12258	
						WVTR g/m²	24,984	23,18	24,516	

Tulokset:									
	Pvm	15.12	16.12	17.12.200	18.12				
	Klo	14.26	14.47	14.19	14.47				
	kp 9	83,1013	83,1943	83,2813	83,3679	Erotus 1	Erotus 2	Erotus 3	
		79,3829	79,4803	79,5691	79,6588	0,093	0,087	0,0866	
		78,1171	78,2052	78,2898	78,3759	0,0974	0,0888	0,0897	
		59,5858	59,6745	59,7608	59,8476	0,0881	0,0846	0,0861	
		60,1507	60,2392	60,3227	60,4097	0,0887	0,0863	0,0868	
						0,0885	0,0835	0,087	
						KA	0,09114	0,08604	0,08724
						WVTR g/m²	18,228	17,208	17,448
	Pvm	15.12	16.12	17.12.200	18.12				
	Klo	14.29	14.52	14.23	14.50				
	kp 10	75,8539	75,9626	76,0665	76,1701	Erotus 1	Erotus 2	Erotus 3	
		82,3401	82,4444	82,5454	82,6471	0,1087	0,1039	0,1036	
		80,0819	80,1841	80,2821	80,3821	0,1043	0,101	0,1017	
		79,3633	79,4698	79,5689	79,6689	0,1022	0,098	0,1	
		63,2248	63,3255	63,4213	63,5173	0,1065	0,0991	0,1	
						0,1007	0,0958	0,096	
						KA	0,10448	0,09956	

Nopeus									
linna/kaasu	26:1								
etäisyys	12								
virtaus	700								
Nopeus	ref.	50	75	100	200				
LST	90	170	150	160	150				
CAW	98,7	66,6	64,6	70,1	80,5				
WVTR	21,27	19,99	19,76	20,86	22,24				
GSM	20,84	21,11	20,47	21,30	20,87				

linna/kaasu									
nopeus	100								
etäisyys	12								
virtaus	700								
linna/kaasu	ref.	24,1	26,1	26,1	28,1				
LST	90	190	160	160	80				
CAW	98,7	76,2	70,1	76,3					
WVTR	21,27	20,42	20,86	17,63					
GSM	20,84	20,77	21,30	19,94					

Etäisyys									
nopeus	100								
linna/kaasu	26:1								
virtaus	700								
Etäisyys	ref.	6	12	18					
LST	90	100	160	120					
CAW	98,56	75,13	69,99	76,60					
WVTR	21,27	19,6	20,86	20,29					
GSM	20,84	21,13	21,30	19,88					

Virtaus									
nopeus	100								
linna/kaasu	26:1								
etäisyys	12								
Virtaus	ref.	500	700						
LST	90	100	160						
CAW	98,7	75,1	70,1						
WVTR	21,27	23,22	20,86						
GSM	20,84	21,51	21,30						

CAW/ Nopeus									
linna/kaasu	26:1								
etäisyys	12								
virtaus	700								
Nopeus	ref.	50	75	100	200				
98,6	67,9	63,3	70,5	78,5					
97,2	67,4	66,5	69,1	81,1					
99,6	66,3	64,4	68,9	79					
98,3	66,2	64,8	71,0	79,8					
97,7	66,5	67,5	70,4	82,8					
99,2	65,1	64,4	70,4	79					
99,3	65,8	64,4	69,6	82,1					
99,5	67,3	61,8	70,9	81,3					
keskiarvo	98,7	66,6	64,6	70,1	80,5				
0,88	0,92	1,76	0,80	1,60					

CAW/ linna/kaasu									
nopeus	100								
etäisyys	12								
virtaus	700								
linna/kaasu	ref.	24,1	26,1	28,1					
98,6	77,1	70,5	76,8						
97,2	75,7	69,1	77						
99,6	75,6	68,9	77,6						
98,3	77,6	71,0	76						
97,7	76,2	70,4	75,9						
99,2	76,8	70,4	76,3						
99,3	75	69,6	76,3						
99,5	75,7	70,9	74,7						
keskiarvo	98,7	76,2	70,1	76,3					
0,88	0,88	0,80	0,86						

CAW/ Etäisyys									
nopeus	100								
linna/kaasu	26:1								
virtaus	700								
Etäisyys	ref.	6	12	18					
98,6	75,1	70,5	76,3						
97,2	75,1	69,1	76,5						
99,6	74,8	68,9	77,0						
98,3	75,9	71,0	76,0						
97,7	75,0	70,4	76,0						
99,2	75,0	70,4	76,9						
99,3	75,0	69,6	77,5						
99,5	75,1	70,9	77,9						
keskiarvo	98,6	75,1	70,0	76,6					
0,88	0,33	0,80	0,69						

WVTR/ Virtaus									
nopeus	100								
linna/kaasu	26:1								
etäisyys	12								
Virtaus	ref.	500	700						
98,6	80,8	70,5							
97,2	78,9	69,1							
99,6	77,4	68,9							
98,3	78,1	71,0							
97,7	77,1	70,4							
99,2	78,9	70,4							
99,3	78,5	69,6							
99,5	79,2	70,9							
keskiarvo	98,7	75,1	70,1						
0,88	1,15	0,80							

WVTR/ Nopeus									
linna/kaasu	26:1								
etäisyys	12								
virtaus	700								
Nopeus	ref.	50	75	100	200				
21,37	20,68	21,33	21,17	22,26					
21,21	19,75	19,18	20,74	22,21					
21,24	19,54	18,76	20,68	22,26					
keskiarvo	21,27	19,99	19,76	20,86	22,24				
0,08	0,61	1,38	0,27	0,02					

WVTR/ linna/kaasu									
nopeus	100								
etäisyys	12								
virtaus	700								
linna/kaasu	ref.	24,1	26,1	28,1					
21,37	20,37	21,17	18,23						
21,21	20,57	20,74	17,21						
21,24	20,33	20,68	17,45						
keskiarvo	21,27	20,42	20,86	17,63					
0,08	0,13	0,27	0,53						

WVTR/ Etäisyys									
nopeus	100								
linna/kaasu	26:1								
virtaus	700								
Etäisyys	ref.	6	12	18					
21,37	19,43	21,17	20,90						
21,21	18,66	20,74	19,91						
21,24	19,08	20,68	20,05						
keskiarvo	21,27	19,06	20,86	20,29					
0,08	0,39	0,27	0,53						

WVTR/ Virtaus									
nopeus	100								
linna/kaasu	26:1								
etäisyys	12								
Virtaus	ref.	500	700						
21,37	23,36	21,17							
21,21	23,14	20,74							
21,24	23,17	20,68							
keskiarvo	21,27	23,22	20,86						
0,08	0,12	0,27							

GSM/ Nopeus									
linna/kaasu	26:1								
etäisyys	12								
virtaus	700								
Nopeus	ref.	6	7	8	1	2			
20,84	21,11	20,47	21,30	20,87					

GSM/ linna/kaasu									
nopeus	100								
etäisyys	12								
virtaus	700								
linna/kaasu	ref.	24,1	26,1	28,1					
20,84	20,77	21,30	19,94						
0,98	0,76	0,68	1,18						

GSM/ Etäisyys									
nopeus	100								
linna/kaasu	26:1								
virtaus	700								
Etäisyys	ref.	6	12	18					
20,84	21,13	21,30	19,88						
0,98	0,42	0,68	1,28						

GSM/ Virtaus									
nopeus	100								
linna/kaasu	26:1								
etäisyys	12								
Virtaus	ref.	500	700						
20,84	21,51	21,30							
0,98	0,83	0,68							

Appendix 3. PP flame

Appendix 4. PP flame WVTR Appendix 5. Corona

Energiä- ja prosessiteknikan laitos
Papertekniikan ja polymeeriteknikan osasto

TAMPEREEN TEKNILLINEN YLIOPISTO

Vesihöyrynläpäisyvyys ASTM E96

Työn tilaaja:	Mikko Tuominen							
Projektitunnus:	WVTR PP							
Näytteet/koalit:								
Standardi/metodit:	Lämpötila (°C): 38 Suhteellinen kosteus (% RH): 90							
Laboratorion tyyppi:								
Työn suorittaja / valmis:								
Tulokset:								
Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00				
np 1-1	73.8630	73.8038	73.9628	74.0195				
A	76.3707	76.1881	76.4761	76.3006				
B	69.1687	69.2225	69.2897	69.3348				
	76.5614	76.6112	76.6701	76.7261				
	73.0868	73.1468	73.2024	73.2578				
					Erotus 1	Erotus 2	Erotus 3	
					0.04896	0.0591	0.0366	
					0.03786	0.0376	0.0345	
					0.05721	0.0569	0.0545	
					0.05976	0.0589	0.058	
					0.037	0.0361	0.0333	
					0.03808	0.03972	0.0378	
					WVTR g/m²	11.616	11.944	11.55
								11.7183
								0.200573
Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00				
np 2	74.5261	75.5152	74.6841	74.7333				
B	66.1749	66.4444	66.3312	66.6147				
	83.4887	83.3506	83.4268	83.4996				
	53.9963	59.0388	59.1258	59.1865				
	79.1641	79.2264	79.2994	79.3742				
					Erotus 1	Erotus 2	Erotus 3	
					0.04804	0.0713	0.0713	
					0.0834	0.0868	0.0833	
					0.07438	0.0713	0.0718	
					0.0714	0.0713	0.0705	
					0.07476	0.073	0.0748	
					0.07438	0.07362	0.0748	
					WVTR g/m²	14.8782	16.124	14.968
								14.9991
								0.123791

Tulokset:

Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00				
np 3	72.1402	72.1612	72.2507	72.3098	Erotus 1	Erotus 2	Erotus 3	
C	61.7123	61.7659	61.8268	61.8913	0.0612	0.0595	0.0591	
	69.3334	69.3741	69.4343	69.4938	0.06432	0.0639	0.0635	
	61.1876	62.2407	62.3003	62.3613	0.06094	0.0602	0.0593	
	66.3321	66.3705	66.4311	66.4923	0.06972	0.0696	0.0695	
					0.0654	0.0651	0.0653	
					0.0631	0.06096	0.06022	
WVTR g/m²	12.6192	12.190	12.044	12.2861				0.29868
KA								
Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00				
np 4	71.8040	71.8728	71.9387	72.0091	Erotus 1	Erotus 2	Erotus 3	
D	64.9394	64.9933	64.9544	64.9264	0.06231	0.0641	0.0724	
	62.6256	62.6772	62.7315	62.8234	0.08868	0.0611	0.072	
	62.1177	62.1973	62.2531	62.3180	0.07752	0.0642	0.0705	
	65.6216	65.6917	65.7583	65.8322	0.08331	0.0882	0.0715	
					0.08412	0.0868	0.0739	
					0.08232	0.0856	0.0725	
WVTR g/m²	16.6464	12.977	14.465	14.6955				1.847731
KA								
Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00				
np 5	68.1896	68.1859	68.2431	68.3011	Erotus 1	Erotus 2	Erotus 3	
E	62.0571	62.3651	62.4234	62.4832	0.05332	0.0572	0.058	
	63.9203	63.9159	63.9159	63.9188	0.06288	0.0603	0.0618	
	60.5076	60.4074	60.4667	60.5266	0.0634	0.0601	0.0604	
	67.8353	67.8942	67.8437	67.9063	0.05978	0.0593	0.0595	
					0.06094	0.0613	0.0604	
					0.06084	0.05988	0.06114	
WVTR g/m²	12.188	11.996	12.228	12.1307				0.194212
KA								

Tulokset:

Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00		Erotus 1	Erotus 2	Erotus 3
np 6	61.2644	61.3309	61.4075	61.4837		0.0788	0.0784	0.0784
P	75.5481	75.6137	75.6875	75.7594		0.07872	0.0788	0.0719
	61.9483	62.0188	62.1264	62.2214		0.10238	0.0964	0.091
	65.4323	65.4972	65.5721	65.6480		0.07764	0.0749	0.0759
	58.9587	59.0659	59.1513	59.2358		0.09144	0.0854	0.0845
					KA	0.08899	0.08102	0.08074
					WVTR g/m²	17.1894	16.204	16.348
							16.5365	
								0.930947
Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00		Erotus 1	Erotus 2	Erotus 3
np 7	78.6503	78.7318	78.8177	78.9083		0.03138	0.0328	0.0331
G	69.8411	69.7675	69.8939	70.0683		0.03331	0.0384	0.0324
	75.0502	75.0505	75.2335	75.4372		0.0332	0.0476	0.0488
	73.1873	73.0625	72.9847	73.2348		0.03344	0.0562	0.053
	77.0883	76.8537	76.8664	76.9513		0.03308	0.0331	0.0331
					KA	0.05488	0.05138	0.05268
					WVTR g/m²	48.332	42.8892	41.6156
							423.909	
								9.402012
Pum	27.1.10	28.1.10	29.1.10	30.1.10				
Kio	17.00	13.30	14.00	15.00		Erotus 1	Erotus 2	Erotus 3
np 8	58.8360	59.8228	59.8330	59.8841		0.03328	0.0526	0.0531
P	72.1071	72.1192	72.2048	72.2930		0.03332	0.0384	0.0324
	50.5746	50.6238	50.6702	50.7251		0.0332	0.0476	0.0488
	67.9761	68.0223	68.0765	68.1313		0.03344	0.0562	0.053
	60.7629	60.8228	60.8839	60.9370		0.03308	0.0331	0.0331
					KA	0.05488	0.05138	0.05268
					WVTR g/m²	16.9728	10.516	10.636
							10.6768	
								0.288184

Tulokset:

Pvm	27.1.10	28.1.10	29.1.10	30.1.10					
Kio	17.00	13.30	14.00	15.00					
np 9	64.9365	64.9783	64.8948	64.8942		Erotus 1	Erotus 2	Erotus 3	
I	61.1540	61.0009	60.9611	60.9216		0.05828	0.0583	0.0594	
	65.9246	65.8471	65.8032	65.8648		0.068	0.068	0.0686	
	66.7187	66.7657	66.8257	66.8839		0.0688	0.06	0.0682	
	60.7133	60.7644	60.8241	60.8832		0.06108	0.0597	0.0565	
KA						0.05786	0.0578	0.05732	
WVTR g/m²			11.5728	11.58	11.504	11.5523			0.041955

Pvm	27.1.10	28.1.10	29.1.10	30.1.10					
Kio	17.00	13.30	14.00	15.00					
np 10	68.7456	68.8458	68.9321	69.0277		Erotus 1	Erotus 2	Erotus 3	
J	62.8809	62.9689	63.0278	63.1207		0.12024	0.0883	0.0956	
	61.1887	61.1752	61.3876	61.4961		0.1182	0.1111	0.1128	
	74.0881	74.1881	74.2389	74.2957		0.11278	0.1124	0.1075	
	64.9186	65.0373	65.1677	65.3062		0.1064	0.0886	0.0716	
KA						0.14244	0.1304	0.1385	
WVTR g/m²			24.9472	20.236	21.368	21.9837			2.168408

Pvm	27.1.10	28.1.10	29.1.10	30.1.10					
Kio	17.00	13.30	14.00	15.00					
np 11	67.8884	67.8675	67.8184	67.8610		Erotus 1	Erotus 2	Erotus 3	
K	62.1511	62.1316	62.3966	62.4740		0.14421	0.1484	0.1484	
	66.9697	66.1981	66.2638	66.2746		0.081	0.0782	0.0777	
	73.7181	73.8438	76.0173	76.0912		0.10728	0.0947	0.0793	
	59.1451	59.2863	59.4788	59.6334		0.07088	0.0599	0.0571	
KA						0.10648	0.1083	0.11794	
WVTR g/m²			12.1514	12.169	11.8158				1.18994
			23.0272	23.86	22.716	29.7077			

Tulokset:					
Pvm	27.1.10	28.1.10	29.1.10	30.1.10	
Kio	17.00	19.30	14.00	15.00	
np 11	68.8307	68.5772	68.6931	68.7298	
L	64.3022	64.3999	64.5993	65.3089	
	62.1759	62.3945	62.4404	62.5287	
	61.1009	61.1792	61.2000	61.5232	
	63.8953	63.4607	63.8356	63.6110	
KA					
WVTR g/m²		27.4176	26.896	26.804	0.416502
Erotus 1	Erotus 2	Erotus 3			
0.0798	0.0739	0.0768			
0.35592	0.3995	0.3486			
0.09408	0.0861	0.0885			
0.07718	0.0746	0.0746			
0.07848	0.0751	0.0752			
0.13709	0.13438	0.13302			
WVTR g/m²		27.4176	26.896	26.804	0.416502
KA					
Erotus 1	Erotus 2	Erotus 3			
0.0798	0.0739	0.0768			
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0.07718	0.0746	0.0746			
0.07848	0.0751	0.0752			
0.13709	0.13438	0.13302			
WVTR g/m²		27.4176	26.896	26.804	0.416502

LDPE/ Teho 3000 W

nopeus	25	50	100
teho/ala	ref.	240	120
WVTR	21.37	19.62	24.98
	21.21	18.45	23.18
	21.24	18.22	24.52
keskiarvo	21.27	18.76	24.23
	0.08	0.75	0.94
			2.75

LDPE/ Teho 60 Wmin/(m2)

nopeus	50	100	3000
teho/ala	ref.	1500	3000
WVTR	21.37	20.68	16.89
	21.21	19.75	21.53
	21.24	19.54	16.66
keskiarvo	21.27	19.99	18.36
	0.08	0.61	2.75

PP/ Teho 3000 W

nopeus	25	50	100
teho/ala	ref.	240	120
WVTR	14.33	13.08	13.16
	16.20	15.01	23.38
	16.15	15.24	22.72
keskiarvo	15.56	14.45	22.32
	1.07	1.19	1.31

PP/ Teho 60 Wmin/(m2)

nopeus	50	100	3000
teho	ref.	1500	3000
WVTR	14.332	22.848	20.86
	16.204	26.856	23.38
	16.148	26.604	22.72
keskiarvo	15.56133	25.436	22.72
	1.055002	2.244813	1.308375

LDPE/ Teho 3000 W

nopeus	25	50	100
teho/ala	ref.	240	120
WVTR	21.37	19.62	24.98
	21.21	18.45	23.18
	21.24	18.22	24.52
keskiarvo	21.27	18.76	24.23
	0.08	0.75	0.94
			2.75

LDPE/ Teho 60 Wmin/(m2)

nopeus	50	100	3000
teho/ala	ref.	1500	3000
WVTR	21.37	20.68	16.89
	21.21	19.75	21.53
	21.24	19.54	16.66
keskiarvo	21.27	19.99	18.36
	0.08	0.61	2.75

PP/ Teho 3000 W

nopeus	25	50	100
teho/ala	ref.	240	120
WVTR	14.33	13.08	13.16
	16.20	15.01	23.38
	16.15	15.24	22.72
keskiarvo	15.56	14.45	22.32
	1.07	1.19	1.31

PP/ Teho 60 Wmin/(m2)

nopeus	50	100	3000
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WVTR	14.332	22.848	20.86
	16.204	26.856	23.38
	16.148	26.604	22.72
keskiarvo	15.56133	25.436	22.72
	1.055002	2.244813	1.308375

Appendix 6. Plasma

LDPE

kaasu	helium				
virtaus	90 l/min				
teho	1,8 kW/ 900 W				
		1	2	3	4
Nopeus		10	20	40	80
I.S.T		70	80	80	80
CAW		59,8	63,7	67,7	71,4
WVTR		26,29	20,16	19,90	20,76
GSM		18,82	19,82	19,44	19,02

WWTR/ LDPE

kaasu	helium				
virtaus	90 l/min				
teho	1,8 kW/ 900 W				
		1	2	3	4
Nopeus		10	20	40	80
		28,74	20,82	20,62	22,15
		26,49	20,96	20,77	21,25
		23,63	18,71	18,31	18,87
Keskiarvo		26,29	20,16	19,90	20,76
		2,56	1,26	1,38	1,70

GSM/ LDPE

kaasu	helium				
virtaus	90 l/min				
teho	1,8 kW/ 900 W				
		1	2	3	4
Nopeus		10	20	40	80
		18,23	20,82	18,92	17,60
		18,49	20,46	19,75	19,52
		19,08	19,26	19,23	18,49
		19,77	19,68	20,35	20,15
		18,52	18,86	18,92	19,35
Keskiarvo		18,82	19,82	19,44	19,02
		0,61	0,81	0,61	0,99

PP

kaasu	helium				
virtaus	90 l/min				
teho	1,8 kW/ 900 W				
		9	10	11	12
Nopeus		10	20	40	80
I.S.T		90	100	100	100
CAW		74,1	79,6	80,7	85,7
WVTR		17,14	13,68	18,74	16,00
GSM		19,82	19,50	19,76	19,30

WVTR/ PP

kaasu	helium				
virtaus	90 l/min				
teho	1,8 kW/ 900 W				
		9	10	11	12
Nopeus		10	20	40	80
		18,44	14,40	19,79	16,81
		17,65	14,14	19,20	16,60
		15,33	12,48	17,23	14,60
Keskiarvo		17,14	13,68	18,74	16,00
		1,62	1,04	1,34	1,22

GSM/ PP

kaasu	helium				
virtaus	90 l/min				
teho	1,8 kW/ 900 W				
		9	10	11	12
Nopeus		10	20	40	80
		19,12	19,74	20,15	19,85
		20,29	17,11	20,85	17,62
		20,46	20,29	19,37	19,83
		20,38	18,71	19,77	19,69
		18,86	21,66	18,65	19,52
Keskiarvo		19,82	19,50	19,76	19,30
		0,77	1,71	0,83	0,95

LDPE

kaasu	argon				
virtaus	30 l/min				
teho	1,8 kW/ 800 W				
		5	6	7	8
Nopeus		10	20	40	80
I.S.T		70	80	80	80
CAW		61,4	67	68,6	69,6
WVTR		20,29	22,15	20,62	24,19
GSM		18,54	17,59	18,07	18,30

WVTR/ LDPE

kaasu	argon				
virtaus	30 l/min				
teho	1,8 kW/ 800 W				
		5	6	7	8
Nopeus		10	20	40	80
		21,13	22,99	21,66	25,22
		20,90	22,99	21,26	24,97
		18,84	20,45	18,93	22,39
Keskiarvo		20,29	22,15	20,62	24,19
		1,26	1,47	1,47	1,57

GSM/ LDPE

kaasu	argon				
virtaus	30 l/min				
teho	1,8 kW/ 800 W				
		5	6	7	8
Nopeus		10	20	40	80
		18,92	17,09	16,48	19,06
		18,12	18,45	18,25	18,12
		18,42	15,98	17,71	17,80
		17,85	19,17	18,02	17,45
		19,42	17,25	19,89	19,09
Keskiarvo		18,54	17,59	18,07	18,30
		0,63	1,24	1,23	0,74

PP

kaasu	argon				
virtaus	30 l/min				
teho	1,8 kW/ 800 W				
		13	14	15	16
Nopeus		10	20	40	80
I.S.T		90	100	100	100
CAW		76,5	77,6	80,5	87,4
WVTR		18,25	14,90	16,05	25,15
GSM		19,34	19,42	17,55	17,75

WVTR/ PP

kaasu	argon				
virtaus	30 l/min				
teho	1,8 kW/ 800 W				
		13	14	15	16
Nopeus		10	20	40	80
		19,44	15,59	17,59	27,68
		18,58	15,56	15,81	24,33
		16,73	13,56	14,76	23,45
Keskiarvo		18,25	14,90	16,05	25,15
		1,39	1,16	1,43	2,23

GSM/ PP

kaasu	argon				
virtaus	30 l/min				
teho	1,8 kW/ 800 W				
		13	14	15	16
Nopeus		10	20	40	80
		20,09	19,49	17,11	16,69
		18,60	18,82	19,74	17,86
		19,15	19,48	17,34	18,29
		19,11	18,63	15,71	17,89
		19,77	20,71	17,86	18,02
Keskiarvo		19,34	19,42	17,55	17,75
		0,59	0,81	1,46	0,62

- He-plasma: 2000W/920W, 28.4 kHz, 2.2A, n.90 l/min
- Ar-plasma: 1800W/780W, 28.2 kHz, 1.9A, n. 30l/min
- F₁: 100 m/min, 12 mm, 24-1, 700 l/min
- F₂: 100 m/min, 12 mm, 28-1, 700 l/min
- Corona1: 3000 W, 100 m/min
- Corona2: 1500 W, 100 m/min

LDPE												
speed	100											
air/gas	1.24											
gas flow	700											
		1	3	5	7	9	11	16				
		f1cor	f1He	f1Ar	cor+f1	He-f1	Ar-f1	f1+cor2				
I-ST		110	140	140	150	160	150	100				
CAW		53,61	59,24	48,36	76,60	81,90	80,40	60,15				
WTR		14,86	18,76	17,42	19,53	19,19	18,73	22,38				
GSM												

CAW/ LDPE															
speed	100														
air/gas	1.24														
gas flow	700														
CAW/ LDPE	100	speed	1.24	gas flow	700	1	3	5	7	9	11	16			
						f1cor	f1He	f1Ar	corf1	He-f1	Ar-f1	f1+cor2			
							55,04	57,62	48,66	74,35	82,81	80,79	67,022		
							53,89	57,87	50,49	80,95	83,73	81,57	60,143		
							53,90	60,28	49,21	77,42	84,31	82,31	59,912		
WTR/ LDPE	100	speed	1.24	gas flow	700		55,52	58,80	47,46	73,94	81,63	81,83	59,977		
							49,77	59,58	46,24	73,79	80,44	82,68	61,251		
							53,04	60,25	45,43	78,18	81,69	81,30	59,538		
							53,01	60,01	50,35	76,83	80,71	75,25	59,108		
							54,75	59,56	49,03	77,31	79,91	77,46	54,303		
Keskilano	100	speed	1.24	gas flow	700		53,61	59,24	48,36	76,60	81,90	80,40	60,15		
							1,80	1,04	1,84	2,47	1,59	2,63	3,47		

WVTR/ LDPE															
speed	100														
air/gas	1.24														
gas flow	700														
WVTR/ LDPE	100	speed	1.24	gas flow	700	1	3	5	7	9	11	16			
						f1cor	f1He	f1Ar	corf1	He-f1	Ar-f1	f1+cor2			
							13,22	18,50	17,77	19,22	19,23	19,10	23,46		
							15,55	17,06	17,06	19,82	19,11	18,53	21,97		
							15,82	19,03	17,43	19,56	19,23	18,57	21,70		
Keskilano	100	speed	1.24	gas flow	700		14,86	18,76	17,42	19,53	19,19	18,73	22,38		
							1,43	0,38	0,36	0,30	0,07	0,32	0,95		

GSM/ PP															
speed	100														
distance	1.24														
gas flow	700														
GSM/ PP	100	speed	1.24	gas flow	700	1	3	5	7	9	11				
						liekki + KOR	liekki + He	liekki + Ar	KOR + liekki	He + liekki	Ar + liekki				
							19,65	19,31	19,80	17,63	17,65	20,00			
							17,72	19,48	18,85	18,60	17,29	19,06			
							18,88	19,52	18,46	17,74	21,03	19,62			
Keskilano	100	speed	1.24	gas flow	700		19,69	20,32	18,57	17,69	18,22	19,22			
							19,35	19,91	19,25	19,26	18,94	20,22			
							19,06	19,71	18,98	18,18	18,62	19,62			

LDPE												
speed	100											
air/gas	1.28											
gas flow	700											
		2	4	6	8	10	12	17				
		f1cor	f1He	f1Ar	corf1	He-f1	Ar-f1	f1+cor2				
I.S.T		80	70	80	100	80	90					
CAW		35,08	55,36	47,75	78,77	79,35	76,01					
WTR		19,5392	25,78005	16,62822	0,0901767	30,1431	19,29779	21,69				
GSM												
		#DIV/0!										

CAW/ LDPE														
speed	100													
air/gas	1.28													
gas flow	700													
CAW		2	4	6	8	10	12	17						
		f1cor	f1He	f1Ar	corf1	He-f1	Ar-f1	f1+cor2						
		39,81	55,06	52,31	76,316	79,27	75,38	50,434	46,47					
		33,28	57,26	40,39	75,242	80,07	74,37	46,47						
		30,98	52,25	41,98	79,15	80,62	71,50	51,49						
		34,90	58,95	45,53	80,365	81,23	76,72	48,875	46,017	78,85	48,165	41,254		
		38,20	53,39	49,25	81,49	78,19	78,85	46,017						
		36,85	57,45	46,28	79,917	78,06	78,83	48,165						
		34,62	54,56	54,49	78,028	78,52	76,44	41,254						
		32,02	53,95	51,74	79,634	78,85		60,89						
Keshano		35,08	55,36	47,75	78,77	79,35	76,01	49,20						
		3,05	2,30	5,06	2,11	1,17	2,59	5,67						

Appendix 8. Treatment order PP

He-plasma: 2000W/920W, 28.4 kHz, 2.2A, n.90 l/min
Ar-plasma: 1800W/780W, 28.2 kHz, 1.9A, n. 30 l/min
F₁: 100 m/min, 12 mm, 24:1, 700 l/min
F₂: 100 m/min, 12 mm, 28:1, 700 l/min
Corona1: 3000 W, 100 m/min
Corona2: 1500 W, 100 m/min

PP															
speed	100														
air/gas	1.24														
gas flow	700														
		1	3	5	7	9	11	14							
		fl+cor 2	fl+He	fl+Ar	cor+fl	He+fl	Ar+fl	fl+cor 2							
IST	120	140	130	160	170	160	130								
CAW	64.87	70.50	63.08	97.14	94.60	85.46	56.18								
WTR	19.71	12.89	11.67	12.07	11.29	13.63	18.37								
GSM	19.06	19.71	18.98	18.18	18.62	19.62									

CAW/PP															
speed	100														
air/gas	1.24														
gas flow	700														
		1	3	5	7	9	11	14							
		fl+cor 2	fl+He	fl+Ar	cor+fl	He+fl	Ar+fl	fl+cor 2							
CAW	63.649	69.347	61.143	95.707	93.318	85.67	56.78								
	66.281	73.618	62.892	97.962	92.703	86.444	55.452								
	65.063	70.569	62.913	96.473	95.787	81.289	56.9								
	65.572	69.531	64.135	100.071	95.171	83.198	54.692								
	65.307	70.967	64.692	98.677	92.621	83.326	53.959								
	66.61	70.123	65.027	100.514	95.64	85.504	56.008								
	61.406	69.359	62.229	96.288	95.724	83.349	59.463								
	65.077		61.571	91.399	95.801	86.869									
Keskivno	64.87	70.50	63.08	97.14	94.60	85.46	56.18								
	1.66	1.51	1.43	2.91	1.45	2.41	1.80								

WTR/PP															
speed	100														
air/gas	1.24														
gas flow	700														
		1	3	5	7	9	11	14							
		fl+cor 2	fl+He	fl+Ar	cor+fl	He+fl	Ar+fl	fl+cor 2							
	20.852	13.216	11.86	11.728	11.364	13.132	22.12								
	20.108	13.204	12.544	12.2	11.56	15.148	16.42								
	18.184	12.264	10.6	12.292	10.936	12.6	16.58								
Keskivno	19.71	12.89	11.67	12.07	11.29	13.63	18.37								
							3.25								

GSM/PP															
speed	100														
distance	1.24														
gas flow	700														
		1	3	5	7	9	11								
		fl+He+cor	fl+He	fl+Ar	cor+fl	He+fl	Ar+fl								
	19.66	19.31	19.80	17.63	17.65	20.00									
	17.72	19.48	18.85	18.60	17.29	19.06									
	18.88	19.52	18.46	17.74	21.03	19.62									
	19.69	20.32	18.57	17.69	18.22	19.22									
	19.35	19.91	19.25	19.26	18.94	20.22									
Keskivno	19.06	19.71	18.98	18.18	18.62	19.62									

PP															
speed	100														
air/gas	1.28														
gas flow	700														
		2	4	6	8	10	12	15							
		fl+cor 2	fl+He	fl+Ar	cor+fl	He+fl	Ar+fl	fl+cor 2							
IST	100	90	100	110	100	100	100								
CAW	57.13	56.17	53.37	84.89	67.47	62.76	57.23								
WTR	12.89	12.11	13.63	11.40	14.20	18.41									
GSM	20.12	19.58	18.78	19.54	18.56	19.21									

CAW/PP															
speed	100														
air/gas	1.28														
gas flow	700														
		2	4	6	8	10	12	15							
		fl+cor 2	fl+He	fl+Ar	cor+fl	He+fl	Ar+fl	fl+cor 2							
CAW	53.495	56.005	52.756	76.114	66.362	67.864	59.615								
	59.4	57.85	54.915	90.537	71.459	66.505	55.038								
	58.9	56.441	51.951	79.134	67.912	63.008	56.212								
	58.49	56.798	52.103	80.587	66.208	63.324	57.743								
	54.482	57.967	56.564	96.325	66.083	59.853	57.423								
	57.135	52.685	53.894	92.215	68.041	59.792	58.188								
	58.507	55.628	55.821	81.488	67.849	60.873	56.372								
	56.651	55.955	48.927	82.725	65.841	60.89									
	57.13	56.17	53.37	84.89	67.47	62.76	57.23								
	2.15	1.65	2.47	7.18	1.85	3.04	1.50								

WVTR/pp															
speed	100														
air/gas	1.28														
gas flow	700														
		3	4	6	8	10	12	15							
		fl+cor 2	fl+He	fl+Ar	cor+fl	He+fl	Ar+fl	fl+cor 2							
	13.216	12.232	14.396	11.36	14.216	18.04366									
	13.204	12.496	14.124	11.788	14.712	18.4192									
	12.264	11.592	12.36	11.064	13.676	18.76									
Keskinoro	12.89	12.11	13.63	11.40	13.676	18.41									

Appendix 9 Time and conditions

	PP										LDPE									
	He 10	He 40	Ar 10	Ar 40	f1 24:1	f1 28:1	corona 25	corona 100			He 10	He 40	Ar 10	Ar 40	f1 24:1	f1 28:1	corona 25	corona 100		
div.	71,074	84,806	80,987	85,198	82,343	76,418	81,986	81,5			59,879	68,476	62,59	66,716	74,943	80,733	56,028	67,377		
	70,86	85,335	80,779	85,075	82,62	75,45	81,79	81,93			61,72	68,90	60,872	67,226	75,82	80,50	55,38	66,74		
	70,35	85,05	80,05	85,23	81,14	75,93	82,46	80,73			60,00	67,26	62,02	67,69	74,42	80,53	56,01	66,91		
	71,728	85,31	81,32	85,11	81,282	76,78	82,72	80,565			59,80	68,70	61,58	67,48	75,168	80,006	55,194	67,623		
	72,498	83,961	80,349	85,515	81,749	76,433	82,895	80,374			60,031	68,226	62,534	66,209	75,665	80,734	55,461	66,645		
	71,077	84,612	81,584	85,567	82,378	77,026	81,679	80,45			60,091	68,684	62,031	67,866	75,375	81,124	55,217	66,853		
	72,404	85,104	81,213	84,497	80,765	77,12	81,84	81,821			60,854	67,355	60,696	66,712	75,719	80,013	55,576	66,917		
	71,23	85,985	81,414	85,661	81,67	76,292	81,932	80,906			61,658	69,283	61,355	67,423	76,1	80,361	55,235	66,644		
	71,65	85,82	80,682	85,033	82,34		81,62	81,32			61,09	68,222	62,091	67,21	75,67	80,48	55,59	66,47		
	71,48	85,32		86,29			81,97	82,45			60,81	68,99	61,93	67,18	74,82		55,46	67,21		
				84,99														66,271		
	average	71,43	85,13	80,93	85,32	81,81	76,43	82,09	81,20		60,59	68,41	61,77	67,17	75,37	80,50	55,52	66,94		
	div.	0,67	0,58	0,51	0,48	0,65	0,56	0,44	0,71		0,73	0,67	0,64	0,50	0,52	0,35	0,30	0,36		

	PP										LDPE									
	He 10	He 40	Ar 10	Ar 40	f1 24:1	f1 28:1	corona 25	corona 100			He 10	He 40	Ar 10	Ar 40	f1 24:1	f1 28:1	corona 25	corona 100		
ref.	59,8	71,3	65,0	73,2	65,4	57,6	68,3	68,1			51,0	57,2	51,4	56,0	63,0	64,3	46,3	57,3		
	24 h																			
	38 °C	78,3	77,3	80,5	84,6	82,1	77,3	82,8	73,3		66,6	66,3	73,5	73,6	64,8	83,1	74,5	79,7		
	25 °C	71,1	87,0	83,5	82,9	84,7	72,3	78,3	79,6		71,3	70,4	73,4	72,0	70,2	79,9	74,4	68,6		
	NTP	71,2	83,8	80,8	85,1	78,0	68,7	80,6	79,3		69,0	72,5	65,7	71,4	66,6	77,0	65,7	70,3		
48 h																				
	38 °C	77,0	89,6	82,2	82,0	80,8	67,2	84,3	79,4		72,6	82,2	76,1	80,4	73,9	81,3	75,2	77,3		
	25 °C	72,6	81,6	83,3	85,8	83,4	79,6	82,8	82,2		66,9	72,1	66,9	74,2	72,9	80,2	66,8	71,5		
	NTP	68,3	85,5	76,0	81,8	78,8	77,8	81,5	82,9		71,7	76,5	69,4	71,6	70,0	77,6	67,8	70,2		
1 w																				
	38 °C	84,2	88,3	95,1	90,1	80,7	73,3	86,2	85,9		76,9	85,3	76,7	86,4	75,6	79,5	83,4	83,2		
	25 °C	73,5	86,2	82,1	86,6	84,8	67,2	83,9	83,6		69,1	78,1	69,4	77,1	73,0	77,1	71,8	73,5		
	NTP	83,3	72,6	82,3	84,1	77,1	78,0	83,9	85,1		70,1	76,2	72,1	74,5	72,0	78,9	70,1	72,1		
1 m																				
	38 °C	92,2	95,4	95,9	99,7	80,3	84,8	88,7	94,7		80,6	90,7	84,3	93,8	85,5	80,8	82,5	89,4		
	25 °C	83,4	89,4	89,6	92,8	90,2	84,4	87,8	89,4		72,3	85,4	74,5	83,0	79,9	81,9	73,5	78,1		
	NTP	82,2	90,4	89,9	92,0	89,0	84,7	94,3	88,5		73,4	80,9	73,3	82,7	77,5	78,2	79,0	77,8		

Appendix 10 Tropical conditions

38 °C RH 90 % 25.03.2010		PP/CAW								LDPE/CAW							
24 h		He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100
		78,991	77,178	78,298	84,512	81,971	77,424	83,391	67,762	68,712	63,036	72,913	74,051	64,355	83,488	72,059	78,228
		77,671	77,172	79,678	83,607	81,822	76,612	83,142	73,218	66,749	64,218	72,858	73,809	60,435	83,453	73,776	78,424
		78,359	77,231	80,987	84,387	82,354	77,473	83,628	77,318	64,5	65,303	74,357	74,172	63,311	82,774	77,822	79,159
		78,818	76,888	83,216	84,859	82,247	76,894	81,875	76,046	65,593	65,564	73,621	73,161	65,158	82,687	73,991	82,527
		78,348	77,113	80,779	85,56	82,004	77,624	82,83	75,757	67,221	65,197	74,434	72,759	66,464	82,781	74,822	80,908
		77,107	77,885	80,05	83,899	82,525	77,482	82,742	75,652	67,095	66,461	73,656	74,408	68,016	83,348	75,866	80,3
		78,735	77,26	81,32	84,691	82,647	77,292	82,707	72,635	68,003	68,01	74,089	73,62	68,063	82,461	76,049	79,882
		78,666	76,946	80,349	86,869	81,689	77,197	83,159	70,278	68,805	62,89	72,548	71,79	63,771	83,61	76,304	81,375
			77,565	79,453	84,654	82,13	77,645	82,33	71,611	66,207	70,637	73,238	73,826	62,246	82,913	72,683	81,752
			77,55		83,947	81,785	77,374	82,402	72,637	63,194	71,397	73,472	74,493	65,888		71,227	77,344
					83,277	81,86											76,698
Average		78,34	77,28	80,46	84,57	82,09	77,30	82,82	73,29	66,61	66,27	73,52	73,61	64,77	83,06	74,46	79,69
div.		0,64	0,31	1,38	0,99	0,32	0,33	0,53	2,96	1,80	2,93	0,64	0,83	2,45	0,42	2,09	1,88
ref.		71,43	85,13	80,93	85,32	81,81	76,43	82,09	81,20	60,59	68,41	61,77	67,17	75,37	80,50	55,52	66,94
		-6,90	7,85	0,47	0,75	-0,28	-0,87	-0,73	7,91	-6,01	2,14	-11,75	-6,44	10,60	-2,56	-18,94	-12,75

38 °C RH 90 % 26.03.2010		PP/CAW								LDPE/CAW							
48 h		He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100
		74,58	87,273	80,938	80,252	81,702	64,411	86,174	76,095	70,989	78,625	75,584	80,547	71,99	83,205	73,69	77,972
		75,779	89,16	83,85	84,135	81,657	67,941	86,552	78,841	74,251	82,331	75,575	81,973	73,224	82,523	75,931	76,064
		74,156	89,781	81,799	83,252	77,96	69,34	88,256	81,098	74,278	78,873	75,016	83,38	74,912	83,758	76,281	77,318
		73,975	89,648	81,845	82,323	74,743	69,113	85,337	76,815	72,44	81,189	79,842	78,222	73,937	81,199	74,617	77,807
		76,448	90,924	81,225	80,085	82,647	67,415	84,522	77,325	72,683	81,955	77,303	78,99	74,127	80,427	73,593	77,771
		80,814	89,086	80,767	83,305	70,005	82,742	80,07		71,631	83,652	79,145	78,366	74,485	79,694	74,755	78,074
		80,851	89,796	81,241	83,091	81,73	67,775	83,94	81,4	72,874	86,485	75,521	82,274	75,376	80,263	75,971	75,626
		78,849	92,333	85,39	85,069	82,123	66,176	81,25	81,671	75,185	83,945	75,009	79,395	75,102	81,355	75,195	77,837
			87,505	84,392	78,702	81,943	63,53	80,369	77,99	71,001	83,45	73,842		73,322	81,958	76,964	78,33
			77,506	90,901	80,289	79,399	82,64	66,617	83,141	70,713	81,903	74,381		72,703	78,872	75,435	75,971
Average		77,00	89,64	82,17	81,96	80,79	67,23	84,35	79,44	72,60	82,24	76,12	80,39	73,92	81,33	75,24	77,28
div.		2,69	1,54	1,74	2,18	2,67	2,10	2,57	2,37	1,56	2,36	2,00	1,96	1,10	1,56	1,10	1,00
Comparison		-1,34	12,36	1,71	-2,61	-1,30	-10,07	1,53	6,15	6,00	15,97	2,60	6,78	9,15	-1,73	0,78	-2,41

38 °C RH 90 % 31.03.2010		PP/CAW								LDPE/CAW							
1 vk		He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100
		81,482	88,127	93,278	89,941	81,917	75,602	90,876	86,877	76,743	81,386	75,809	87,727	72,628	75,147	83,909	80,678
		82,128	87,735	96,526	87,724	79,888	77,201	89,358	87,083	77,495	84,067	77,608	86,229	72,552	78,446	83,347	82,617
		82,114	88,089	95,584	87,865	78,682	76,714	86,004	88,263	77,682	84,719	77,167	87,496	71,962	79,256	83,796	82,196
		80,294	88,348	98,508	92,273		74,93	85,718	84,662	77,99	83,494	76,474	86,204	76,499	78,379	85,967	83,44
		81,844	89,189	92,238	90,67		74,248	85,94	84,493	77,574	83,497	76,616	87,008	75,731	76,43	83,589	85,858
		84,471	89,271	93,82	90,095	80,948	71,067	85,307	84,463	78,14	87,381	77,565	86,778	78,955	79,236	82,484	83,295
		86,411	87,836	95,036	89,032	80,981	71,265	81,712	89,59	75,319	89,083	78,224	85,767	77,072	80,11	82,673	84,123
		88,377	85,512	96,67	90,499	81,015	71,856	85,566	84,596	74,109	86,032	74,896	85,98	78,441	82,05	82,807	83,472
		87,4	88,779	94,249	91,908	81,463	70,169	87,07	85,651	75,306	85,984	78,57	85,892	77,096	81,222	83,756	83,543
		86,986	89,702	95,042	90,849	80,959	69,834	84,52	83,203	78,31	87,111	74,232	85,36	74,952	84,822	81,555	82,866
Average		84,15	88,26	95,10	90,09	80,73	73,29	86,21	85,89	76,87	85,28	76,72	86,44	75,59	79,51	83,39	83,21
div.		2,93	1,17	1,83	1,52	1,01	2,76	2,52	2,00	1,45	2,28	1,41	0,78	2,50	2,77	1,17	1,33
Comparison		7,16	-1,38	12,92	8,12	-0,06	6,06	1,86	6,44	4,26	3,03	0,59	6,05	1,67	-1,82	8,15	5,93

38 °C RH 90 % 06.04.2010		PP/CAW								LDPE/CAW							
2 weeks		He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100
			90,606	88,353	87,418	84,045	81,166	90,896	90,351	79,424	80,199	72,976	89,918	74,717	74,885	78,159	78,747
		81,982	88,974	88,495	90,732	86,811	80,242		88,229	77,99	81,979	73,339	86,693	75,025	76,314	80,439	80,348
		82,539	93,731	86,714	92,247	86,7	78,084	92,152	91,918	76,096	85,274	77,367	88,218	75,23	78,102	78,855	82,867
		89,453	92,373	89,628	89,224	87,743	76,648		87,93	76,339	84,246	76,363	87,838	72,848	76,09	80,398	78,742
		87,274	92,086	89,704	92,638	86,187	79,307	93,126	84,674	74,705	84,826	79,244	88,167	74,521	79,606	76,748	80,927
		88,71	95,512	86,456	87,037	85,38	77,752	93,074	87,518	76,145	85,648	77,05	83,971	74,186	77,464	77,839	80,097
		84,588	95,432	87,382	89,613	86,239	75,744	90,857	89,517	77,685	83,175	77,105	87,626	73,121	76,337	78,353	79,672
		88,528	93,561	88,52	88,424	84,118	74,046	90,851	91,029	77,171	86,421	79,806	82,291	70,936	76,897	76,055	81,796
		87,634	91,322	86,907	91,048	82,84	81,904	94,023	88,477	73,641	84,56	79,4	82,202	69,983	78,643	73,789	79,821
		85,418	89,743	89,969	85,253		81,399	89,827	88,673	72,752	87,488	77,557	89,618	70,039		77,05	81,313
			89,404														
Average		86,24	92,33	88,32	89,36	85,56	78,63	91,85	88,83	76,19	84,38	77,02	86,65	73,06	77,04	77,77	80,43
div.		2,74	2,24	1,29	2,38	1,59	2,63	1,46	2,04	2,04	2,14	2,34	2,84	2,05	1,51	2,00	1,32
Comparison		2,09	2,09	4,08	-6,77	-0,72	4,83	5,34	5,64	#REF!	-0,67	-0,89	0,30	0,21	-2,53	-2,47	-5,62

38 °C RH 90 % 25.04.2010		PP/CAW								LDPE/CAW							
1 month		He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100
		92,543	95,622	93,876	94,48	80,174	84,637	88,507	95,206	80,558	90,936	84,855	92,452	81,736	80,769	82,268	87,061
		92,702	95,535	93,713	99,408	80,094	85,346	88,658	94,262	78,887	90,011	83,571	94,198	80,66	80,977	82,432	87,014
		91,982	95,062	95,637	101,017	80,708	85,305	88,334	95,258	81,19	91,089	84,545	93,66	81,167	80,248	82,806	89,15
		92,208	96,093	94,874	98,885	80,69	85,246	90,023	95,309	80,762	90,629	84,356	93,028	87,651	81,111	82,473	89,652
		91,892	95,952	97,095	100,187	81,407	84,925	88,618	93,807	80,673	90,573	84,042	92,455	86,635	81,388	82,233	89,604
		91,557	95,583	94,957	100,894		84,722	88,34	94,904	80,909	91,341	83,766	95,738	87,555	81,016	82,634	90,441
		92,279	95,687	97,316	101,946	79,36	84,218	88,383	94,564	82,129	91,207	84,782	92,078	87,987	80,375	82,985	91,651
		92,605	95,337	97,041	102,008	79,768	84,714	89,146	94,69	81,78	91,217	84,385	95,023	86,913	80,502	82,654	90,013
		92,409	95,194	98,181	100,421	79,946	84,494	89,463	95,355	78,602	90,493		95,702	88,878	80,749	81,978	
		92,147	94,394	96,01	98,19	80,274	84,922	88,299	93,989	80,322	90,161				80,555	82,789	
							84,195	87,975			90,514						
Average		92,23	95,45	95,87	99,74	80,27	84,79	88,70	94,73	80,58	90,74	84,29	93,81	85,46	80,77	82,53	89,45
div.		0,35	0,49	1,52	2,22	0,60	0,40	0,60	0,57	1,12	0,45	0,46	1,42	3,28	0,36	0,31	1,66
Comparison		6,00	3,11	7,55	10,38	-5,29	6,16	-3,15	5,90	4,39	6,36	7,27	7,16	12,40	3,73	4,76	9,00

Appendix 11 Mild conditions

25 °C RH 75 % 25.03.2010																					
24 h	PP/CAW								LDPE/CAW												
	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100					
	70,313	85,396	79,161	79,681	86,587	72,966		77,14	68,913	67,198	70,596	71,596	66,204	80,077	72,977	66,277					
		84,754	85,177		85,741	71,811	80,653	78,439	71,438	67,43	69,22	73,096	67,749	79,771	73,106	66,564					
	72,767	84,145	84,495	79,5	82,68	73,907	80,803	79,397	74,027	68,837	72,157	71,636	71,019	83,631	73,637	68,436					
	71,697	88,652	84,636	80,325	83,41	72,571	75,368	81,964	75,083	71,331	71,256	71,737	73,561	83,043	74,328	69,613					
	71,185	87,527	85,397	81,132	82,06	70,558	77,234	80,747	73,696	72,63	72,899	70,169	67,246	80,742	76,539	71,026					
	73,213	88,627	85,215	83,473	84,127	72,795	77,452	81,797	67,509	72,748	77,025	73,74	69,449	78,195	75,83	71,157					
		88,145	83,1	85,82	85,903	71,357	76,306	79,38	69,818	72,913	78,283	71,93	69,926	77,809	77,048	66,55					
	69,386	88,746	83,062	86,658	87,684	71,826	76,794	77,647	70,669	70,3	79,904	71,418	73,157	78,931	77,449						
	70,951		83,46	86,588	84,494	73,03	80,353	80,242	70,226	69,63	69,885	76,316	71,909	76,582	71,216	68,842					
	69,634		81,584				79,814			70,932	72,391	68,25	71,731		71,831						
Average	71,14	87,00	83,53	82,90	84,74	72,31	78,31	79,64	71,26	70,39	73,36	71,99	70,20	79,86	74,40	68,56					
div.	1,38	1,92	1,96	3,12	1,87	1,02	2,09	1,71	2,53	2,11	3,72	2,13	2,52	2,34	2,21	1,97					
ref.	71,43	85,13	80,93	85,32	81,81	76,43	82,09	81,20	60,59	68,41	61,77	67,17	75,37	80,50	55,52	66,94					
	-0,29	1,87	2,60	-2,42	2,93	-4,12	-3,78	-1,56	10,67	1,99	11,59	4,82	-5,17	-0,63	18,88	1,62					

25 °C RH 75 %																								
26.03.2010		PP/CAW								LDPE/CAW														
48 h	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100								
	70,875	81,682		86,091	81,086		82,435	84,125	67,375	72,432	66,004	73,777	69,554		64,602	71,975								
		82,746		84,642	82,366		83,489	83,912	70,102	70,378	66,797	74,155	72,649	76,976	65,552	68,61								
	74,098	81,919	83,398	87,975	86,403	76,901	86,624	81,686	68,171	72,148	68,519	74,392	73,95	79,251	67,237	69,163								
	74,005	80,447	85,319	86,956	86,808	79,961	81,366	81,471	69,463	73,848	68,844	76,192	75,772	79,657	64,051	70,387								
	73,465	79,969	83,247	89,502	82,191	78,775	81,688	80,508	67,275	71,539	66,919	76,271	75,708	82,486	67,336	71,134								
	75,238	80,615		85,451	82,369	77,861	82,632	80,676	67,199	73,212	64,428	73,065	74,239	81,904	67,95	73,207								
	71,496	81,392	80,269	80,048	81,682	79,201	81,295	80,792	66,622	71,367	68,308	74,041	71,141	82,054	68,55	75,833								
	71,196	82,419	82,198	86,591	84,115	80,447	82,531	82,068	66,688	72,031	67,349	74,865	72,491	79,855	66,649	73,681								
	70,051	82,708	85,647	87,679		81,699	83,531	81,587	64,341	73,471	67,149	75,183	70,72	79,65	67,464	69,417								
		81,825	85,028	87,756	84,026	81,855	82,723	85,23	61,739	70,732	64,392	70,126			68,6	72,037								
			81,28	80,924	82,729					71,735														
Average	72,55	81,57	83,30	85,78	83,38	79,59	82,83	82,21	66,90	72,08	66,87	74,21	72,91	80,23	66,80	71,54								
div.	1,87	0,96	1,97	2,94	1,94	1,75	1,54	1,64	2,41	1,10	1,56	1,76	2,19	1,84	1,58	2,27								
Comparison	1,41	-5,43	-0,23	2,89	-1,37	7,27	4,52	2,57	-4,37	1,69	-6,49	2,22	2,72	0,36	-7,60	2,99								

25 °C RH 75 %																									
31.03.2010																									
1 vk	PP/CAW								LDPE/CAW																
	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100									
	75,214		85,44	88,193	84,352	69,748	80,742											65,964	80,487	71,514	79,686	75,604	75,902	72,831	70,787
	73,671	83,021	82,878	86,488	88,216	70,043	84,468											66,498	77,632	68,628	78,08	70,813	77,896	71,669	71,506
	73,248	82,782	83,585	88,993	87,685	66,017	85,404	85,249										67,726	77,277	70,031	78,246	72,146	81,702	71,385	71,405
	73,218	88,828	82,583	88,273	83,054	66,385	83,22	80,574										67,859	76,905	68,573	77,306	75,637	82,85	72,161	75,311
	70,24	88,996	81,858	86,719	84,199	66,009	83,033	80,889										71,072	76,812	68,652	76,095	74,611	77,688	71,978	76,168
	72,214	87,916	81,934	86,632	86,307	69,437	81,802	84,001										69,495	78,668	69,076	75,645	71,487	75,986	73,361	76,402
	74,663	86,495	80,968	87,611	86,501	67,279	82,719	84,008										71,169	78,55	70,794	75,562	73,262	74,723	73,247	71,901
	70,917	87,175	79,777	84,712	85,502	64,531	84,251	83,279										71,169	79,689	66,655	76,489	72,471	73,719	73,282	74,544
	76,682	84,065	82,008	83,141	80,557	65,255	87,231	84,191										70,462	78,365	69,468	78,773	70,648	74,586	67,006	76,221
	74,842	86,217	79,817	85,381	81,533		86,594	86,913										70,06	77,059	71,027	75,338		75,456	71,327	70,713
Average	73,49	86,17	82,08	86,61	84,79	67,19	83,95	83,64										69,15	78,14	69,44	77,12	72,96	77,05	71,82	73,50
div.	1,98	2,37	1,71	1,80	2,54	2,06	2,06	2,10										1,98	1,24	1,45	1,52	1,94	3,05	1,87	2,43
Comparison	0,94	4,59	-1,21	0,83	1,41	-12,40	1,12	1,43										2,25	6,06	2,57	2,92	0,05	-3,18	5,03	1,95

25 °C RH 75 % 06.04.2010																					
PP/CAW														LDPE/CAW							
2 weeks	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fl 24:1	fl 28:1	corona 25	corona 100					
	74,305	85,041	85,509	89,691	77,39	79,304	85,534	84,832	68,442	74,269	69,496	75,777	73,859	82,252	62,093	70,142					
		85,718	83,275	86,134	79,469	81,589	82,859	83,224	68,089	75,659	70,212	75,745	73,236	81,92	62,634						
	71,679	86,033	82,352	88,737	80,964	80,267	87,522	85,117	68,483	78,115	70,376	77,163	74,81	81,086	65,007	72,748					
	75,841	87,347	82,709	90,055	81,916	79,502	87,485	82,831	67,2	77,737	68,157	78,511	76,573	84,829	66,383	73,395					
	73,075	86,223	81,729	90,129	81,008	78,476	84,371	85,447	68,252	77,969	67,684	77,003	77,466	83,909	64,384	74,517					
	74,379	87,508	83,253	89,399	83,776	78,466	82,889		68,409	74,964	68,892	76,559	73,478	82,761	66,996	76,39					
	74,819	85,506	82,301	88,924	85,741		81,536	83,06	69,029	75,623	67,424	80,01	73,691	82,483	67,695	73,735					
	73,7	83,337	81,358	86,883	85,052	78,799	81,607	81,008	67,153	75,331	68,783	81,547	75,73	82,537	65,868	72,065					
	74,29	82,054	84,157	88,561		80,183	84,246	81,421	70,308	77,064	69,202	80,367	77,186	83,102	67,144	72,95					
	77,062	82,307		86,288		79,932	82,443	80,656	70,129	76,381	69,166	80,49	76,168	83,294	67,125	71,618					
Average	74,35	85,11	82,96	88,48	81,91	79,61	84,05	83,07	68,55	76,31	68,94	78,32	75,22	82,82	65,53	73,06					
div.	1,54	1,94	1,28	1,51	2,83	1,01	2,21	1,80	1,05	1,35	0,98	2,15	1,61	1,05	1,96	1,78					
Comparison	0,86	-1,06	0,88	1,87	-2,88	12,42	0,10	-0,57	-0,60	-1,83	-0,50	1,20	2,26	5,77	-6,29	-0,43					

Appendix 12. Normal conditions

23 °C RH 50 % 25.03.2010		PP/CAW								LDPE/CAW							
24 h		He 10	He 40	Ar 10	Ar 40	fi 24:1	fi 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fi 24:1	fi 28:1	corona 25	corona 100
		71,386	83,843	78,981	84,307	78,228	69,922	80,349	75,631	67,155	72,782	63,576	71,958	66,783	76,461	62,416	68,859
		71,553	88,371	79,674	85,226	78,059	64,407	79,821	78,558	69,505	72,104	66,32	70,845	66,779	77,966	64,49	70,348
		69,85	80,558	81,213	84,599	77,589	64,734	83,566	78,486	67,846	70,845	68,125	72,129	66,63	75,838	64,754	68,85
		70,253	81,541	77,487	83,873	78,508	66,887	83,62	78,411	68,655	72,265	67,503	72,705	66,453	80,496	66,727	68,258
		70,897	84,944	79,713	86,138	78,467	68,749	78,669	78,205	69,482	74,437	67,25	74,258	66,608	76,083	67,122	70,131
		71,541	83,172	81,414	85,747	79,416	68,548	81,712	80,102	71,749	73,915	64,657	69,618	66,103	74,788	67,644	71,968
		71,943	86,13	84,729	88,415	77,441	70,612	76,937	80,808	71,226	71,025	67,294	70,992	66,964	73,098	65,915	72,969
		70,805	86,097	80,682	85,806	76,901	72,818	78,173	80,121	73,519	73,937	65,75	70,792	66,47	77,212	65,816	73,301
		72,171	83,166	83,263	81,967	78,312	69,062	78,224	78,614	65,682	74,433	64,221	69,385	66,406	81,883	65,415	69,741
		70,993	80,303			77,97	70,934	85,044	83,848	65,151	69,524	62,295		66,696	76,018	66,916	68,451
Average		71,16	83,81	80,80	85,12	77,97	68,67	80,61	79,31	69,00	72,53	65,70	71,41	66,59	76,98	65,72	70,29
div.		0,77	2,62	2,20	1,77	0,69	2,68	2,75	2,14	2,67	1,69	1,94	1,53	0,24	2,59	1,55	1,86
Ref.		71,43	85,13	80,93	85,32	81,81	76,43	82,09	81,20	60,59	68,41	61,77	67,17	75,37	80,50	55,52	66,94
		-0,28	-1,32	-0,14	-0,20	-3,84	-7,76	-1,48	-1,90	8,40	4,12	3,93	4,24	-8,78	-3,51	10,21	3,35

23 °C RH 50 % 26.03.2010		PP/CAW								LDPE/CAW							
48 h		He 10	He 40	Ar 10	Ar 40	fi 24:1	fi 28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	fi 24:1	fi 28:1	corona 25	corona 100
		66,877	83,83	75,022	77,718	79,068	78,002	80,929	87,122	69,872	74,176	68,134	70,343	66,931	75,284	63,533	67,095
		69,892	85,045	76,933	80,198	76,887	79,085	81,834	81,899	71,919	76,247	71,046	73,295	68,978	76,687	65,434	71,13
		68,801	86,747	74,927	79,777	79,283	77,596	83,405	83,364	72,787	80,189	70,83	71,036	71,763	74,731	68,578	73,717
		67,763	88,797	73,562	86,31	80,636	78,056	84,932	83,34	72,048	76,618	72,511	70,078	69,721	76,082	65,162	70,599
		65,746	87,593	74,808	84,659	76,864	77,858	81,573	81,485	70,651	76,159	67,692	71,288	69,511	76,95	68,519	71,33
		67,512	85,302	74,547	80,897	77,593	75,947	80,598	80,54	71,789	76,746	68,288	69,905	70,569	78,953	68,593	70,92
		68,006	83,718	74,903	82,854	77,705	75,751	84,569	80,573	71,773	80,32	66,416	73,381	72,725	80,042	68,935	70,322
		68,866	85,819	78,068	81,808	76,657	77,791	78,545	82,991	74,116	75,232	69,613	71,816	68,272	80,334	73,55	68,566
		71,646	84,047	78,285	82,018	83,41	79,559	79,851	83,732	69,887	75,369	69,623	73,244	71,78	78,908	68,661	71,812
		84,203	78,591		79,827	78,266	78,885	83,714		72,039	74,422					67,252	66,581
Average		68,35	85,51	75,96	81,80	78,79	77,79	81,51	82,88	71,69	76,55	69,35	71,60	70,03	77,55	67,84	70,21
div.		1,73	1,73	1,82	2,59	2,12	1,19	2,22	1,93	1,29	2,14	1,91	1,41	1,86	2,07	2,75	2,19
Comparison		-3,09	0,38	-4,97	-3,51	-3,02	1,36	-0,58	1,67	0,00	11,09	8,14	7,58	4,43	-5,34	-2,94	12,33
																	3,27

23 °C RH 50 % 31.03.2010		PP								LDPE							
1 vk		He 10	He 40	Ar 10	Ar 40	liekki 24:1	liekki28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	liekki 24:1	liekki28:1	corona 25	corona 100
		83,558	70,518	83,162	84,157	77,614	77,072	86,041	83,571	70,772	76,815	70,554	74,309	68,66	76,647	70,977	72,898
		81,671	71,257	81,542	81,816	76,887	80,732	83,556	84,255	71,148	75,992	72,326	74,154	73,215	76,984	70,299	72,518
		82,167	73,741	80,384	82,904	76,557	78,086	81,996	86,605	70,566	73,566	73,824	73,87	73,978	77,861	69,419	71,432
		83,25	75,653	82,067	85,396	77,658	78,245	83,179	84,51	70,875	76,187	75,085	74,354	73,092	82,747	69,905	71,558
		81,931	74,071	80,853	85,395	77,205	77,359	81,454	84,919	69,642	76,758	73,243	73,661	74,684	78,494	71,205	69,494
		82,948	73,404	82,689	85,725	77,593	78,227	82,934	86,837	69,707	76,997	72,765	74,945	72,631	76,866	70,42	69,926
		85,866	70,736	82,148	85,57	77,705	79,832	86,689	85,94	69,674	78,153	71,766	77,008	73,268	76,711	69,021	73,279
		82,276	70,594	84,218	85,014	76,657	75,922	84,004	83,492	70,257	75,937	70,145	76,574	71,494	79,843	67,89	73,014
		84,52	73,03	84,367	83,308	77,108	77,601	84,522	85,905	68,677	76,34	71,92	73,187	70,707	81,98	70,975	72,562
		84,733	72,8	81,853	81,646	76,151	76,868	84,235		69,766	75,428	68,879	73,393	67,866	81,255	70,854	74,639
Average		83,29	72,58	82,33	84,09	77,11	77,99	83,86	85,11	70,11	76,22	72,05	74,55	71,96	78,94	70,10	72,13
div.		1,38	1,74	1,31	1,57	0,54	1,41	1,63	1,26	0,75	1,19	1,84	1,29	2,26	2,35	1,05	1,56
Comparison		14,95	-12,93	6,36	2,29	-1,68	0,20	2,35	2,24	-1,58	-0,33	2,70	2,95	1,93	1,39	2,25	1,92

23 °C RH 50 % 06.04.2010		PP								LDPE							
2 weeks		He 10	He 40	Ar 10	Ar 40	liekki 24:1	liekki28:1	corona 25	corona 100	He 10	He 40	Ar 10	Ar 40	liekki 24:1	liekki28:1	corona 25	corona 100
		74,863	89,95	85,31	84,446	82,259	84,423	85,653	89,8	65,113	64,245	72,455	73,614	80,561	75,512	69,76	72,029
		75,736	93,89	77,841	82,6	87,317	80,391	85,34	92,065	64,142	67,17	69,538	73,22	80,362	73,312	70,717	73,676
		74,957	91,425	77,243	83,679	90,723	87,01	87,993	93,56	66,273	72,857	69,853	74,875	81,488	77,247	71,222	72,762
		76,265	89,932	81,256	81,843	88,818	86,329	87,722	94,03	65,474	71,241	69,867	78,869	81,695	80,107	72,424	72,197
		77,997	92,027	77,592	84,223	88,716	84,429	85,331	95,396	66,558	70,011	72,602	76,889	79,814	76,523	73,699	73,497
		74,092	92,861	77,788	84,362	88,37	82,777	86,969	94,054	65,032	70,516	71,343	74,689	79,021	76,098	74,349	71,788
		76,963	95,318	77,016	82,352	85,599	84,035	86,765	93,476	65,793	71,302	72,774	75,089	78,749	77,298	71,4	71,727
		75,668	96,367	81,705	80,828	85,949	81,824	87,021	91,775	68,358	72,319	73,725	75,788	80,215	80,109	73,308	72,119
		75,498	95,129	81,168	77,838	81,454	83,213	87,185	89,069	70,519	70,225	70,942	77,711	79,141	79,317	73,982	71,979
		74,769	97,856	83,579		85,685	79,904	87,774	89,314	67,573	69,496		77,752	77,129		73,443	73,901
Average		75,68	93,48	80,05	82,46	86,49	83,43	86,78	92,25	66,48	69,94	71,46	75,85	79,82	77,27	72,43	72,52
div.		1,15	2,70	2,96	2,14	2,93	2,32	1,00	2,22	1,89	2,55	1,51	1,89	1,37	2,26	1,57	0,89
Comparison		-7,61	20,90	-2,28	-1,63	9,38	5,44	2,91	7,14	-3,62	-6,28	-0,60	1,30	7,86	-1,66	2,33	0,39

23 °C RH 50 % 25.04.2010		PP								LDPE	
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Appendix 13. Time and conditions/ heatseal and hot tack

LDPE

NTP	1 pv	2 vk	1 kk	6kk
Ar 10	80	80	70	70
Ar 40	80	80	60	80
He 10	80	80	60	70
He 40	80	80	60	70
cor 25	80	80	70	70
cor 100	80	80	70	80
ref.	90	90	80	
28:1	80	90	80	80
24:1	160	150	140	180

LDPE

Mild	1 pv	2 vk	1 kk
Ar 10	80	80	60
Ar 40	80	80	60
He 10	70	70	60
He 40	80	80	60
cor 25	80	80	60
cor 100	80	80	70
ref.	90	90	80
28:1	90	90	80
24:1	160	150	140

LDPE

TR	1 pv	2 vk	1 kk
Ar 10	110	90	60
Ar 40	110	80	70
He 10	100	80	60
He 40	100	80	60
cor 25	100	80	70
cor 100	100	80	70
ref.	110	90	70
28:1	110	90	80
24:1	160	160	150

PP

NTP	1 pv	2 vk	1 kk	6kk
Ar 10	100	100	90	100
Ar 40	100	110	80	100
He 10	110	110	90	100
He 40	110	110	80	100
cor 25	100	100	90	100
cor 100	100	100	90	100
ref.	110	110	90	
28:1	110	110	90	90
24:1	160	130	140	170

PP

Mild	1 pv	2 vk	1 kk
Ar 10	110	110	90
Ar 40	110	110	80
He 10	100	100	90
He 40	100	100	80
cor 25	100	110	90
cor 100	100	120	80
ref.	110	110	90
28:1	110	120	100
24:1	160	150	140

PP

TR	1 pv	2 vk	1 kk
Ar 10	100	100	90
Ar 40	100	100	90
He 10	100	110	90
He 40	100	110	90
cor 25	100	100	90
cor 100	100	100	90
ref.	110	110	90
28:1	110	110	100
24:1	160	150	140

	24h	Tropic	Mild	NTP
PE Ar 10	110	100	90	90
PE Ar 40	100	100	90	100
PE He 10	110	100	90	100
PE He 40	120	100	90	100
PE, L 24,1	150	130	130	130
PE,L 28,1	100	90	90	100
PE,C 25	100	100	100	100
PE,C 100	100	100	100	100
Ref	90	80	90	80
PP Ar 10	110	110	110	100
PP Ar 40	110	90	110	110
PP He 10	100	90	90	90
PP He 40	100	90	90	90
PP, L 24,1	140	120	120	110
PP,L 28,1	110	110	90	90
PP,C 25	110	110	90	90
PP,C 100	110	110	110	90
PP Ref	110	110	100	110

Appendix 14. Time and conditions/ hot tack-strength

Hot tack					Hot tack				
LDPE	Tropic	Mild	NTP	24 h	PP	Tropic	Mild	NTP	24 h
PE Ar 10	9,075	9,661	8,587	9,661	PP Ar 10	7,122	7,805	7,708	8,782
	8,098	8,684	9,368	12,186		8,489	8,880	8,536	9,563
	7,317	8,684	8,587	9,563		8,294	7,415	7,657	7,610
	8,880	9,186	9,368	10,833		7,122	7,657	6,048	7,415
	7,317	10,052	9,270	12,200		7,731	8,880	7,546	7,610
aver.	8,137	9,253	9,036	10,889	aver.	7,752	8,127	7,499	8,196
stdev.	0,833	0,604	0,412	1,291	stdev.	0,639	0,701	0,902	0,937
PE Ar 40	8,391	10,540	9,563	16,790	PP Ar 40	7,317	8,782	7,415	23,360
	8,489	11,321	8,098	17,428		6,048	9,563	8,098	19,720
	7,927	9,720	8,489	17,962		6,368	8,927	7,412	10,708
	7,610	9,856	9,270	16,106		9,856	8,263	7,708	14,778
	7,415	10,442	8,317	17,473		7,220	7,927	8,001	10,755
aver.	7,966	10,376	8,747	17,152	aver.	7,362	8,692	7,727	15,864
stdev.	0,421	0,570	0,568	0,642	stdev.	1,496	0,631	0,320	5,588
PE He 10	8,894	9,954	8,001	9,233	PP He 10	7,415	8,098	8,977	7,024
	8,782	9,563	7,805	9,173		7,024	8,391	7,512	7,122
	8,391	8,294	9,543	10,247		6,341	8,782	9,173	6,927
	8,489	10,247	8,076	9,466		8,977	9,052	8,587	9,759
	8,664	8,587	8,635	11,298		7,341	8,294	8,294	6,536
aver.	8,644	9,329	8,412	9,883	aver.	7,420	8,523	8,509	7,474
stdev.	0,206	0,853	0,703	0,899	stdev.	0,968	0,386	0,653	1,297
PE He 40	8,089	9,368	9,446	8,977	PP He 40	8,849	9,563	7,903	7,708
	8,880	10,247	8,880	9,368		6,731	10,052	8,001	6,927
	8,294	10,052	8,122	9,661		6,341	9,415	8,456	6,908
	8,829	10,637	8,415	8,587		8,849	8,782	8,805	7,896
	7,927	11,164	8,196	9,052		8,098	10,012	8,684	7,727
aver.	8,404	10,294	8,612	9,129	aver.	7,774	9,565	8,370	7,433
stdev.	0,432	0,669	0,552	0,407	stdev.	1,179	0,518	0,403	0,476
PE, L 24,1	1,755	2,434	2,044	3,239	PP, L 24,1	5,216	5,216	4,485	4,583
	1,946	2,239	2,434	2,892		6,341	4,337	6,243	4,387
	1,751	2,679	2,630	2,630		5,950	5,755	6,358	6,012
	1,663	2,399	2,337	3,313		6,829	5,559	6,581	4,166
	1,826	3,016	2,648	2,727		6,423	5,266	5,752	5,982
aver.	1,788	2,553	2,419	2,960	aver.	6,152	5,227	5,884	5,026
stdev.	0,105	0,303	0,247	0,304	stdev.	0,609	0,544	0,839	0,899
PE,L 28,1	8,684	10,930	8,684	10,247	PP,L 28,1	6,634	10,052	9,220	8,880
	9,661	11,126	9,368	11,126		6,927	11,614	8,098	8,196
	9,173	9,954	8,903	10,833		6,145	10,833	8,880	10,052
	8,160	9,661	8,196	11,126		8,294	12,981	11,614	10,883
	8,122	10,442	7,903	11,223		6,145	10,466	9,368	6,992
aver.	8,760	10,423	8,611	10,911	aver.	6,829	11,189	9,436	9,001
stdev.	0,662	0,623	0,578	0,399	stdev.	0,885	1,155	1,313	1,529
PE,C 25	7,610	9,759	9,446	11,102	PP,C 25	7,708	8,196	8,782	8,294
	8,089	10,052	8,684	10,930		7,438	7,903	7,903	8,294
	9,075	10,247	8,805	10,930		8,001	8,294	8,489	9,996
	8,489	9,856	9,759	11,126		7,927	8,196	8,001	7,892
	8,001	9,720	8,782	10,930		8,481	8,927	9,367	8,012
aver.	8,253	9,927	9,095	11,004	aver.	7,911	8,303	8,508	8,498
stdev.	0,556	0,220	0,478	0,101	stdev.	0,387	0,378	0,599	0,856
PE,C 100	8,169	9,270	8,782	9,466	PP,C 100	6,243	9,759	8,294	8,489
	6,829	8,684	9,446	9,075		7,317	8,880	7,489	7,805
	7,708	9,173	12,786	9,368		6,048	7,708	7,024	7,903
	8,243	8,831	8,294	10,052		6,071	8,391	7,415	8,387
	7,708	8,782	9,075	9,270		6,657	7,996	7,025	9,563
aver.	7,731	8,948	9,677	9,446	aver.	6,467	8,547	7,449	8,429
stdev.	0,563	0,258	1,789	0,368	stdev.	0,534	0,808	0,519	0,700
PE Ref	10,735	12,102	13,274	12,395 k	PP Ref	11,419	13,079	13,470	11,126
	11,321	13,177	12,052	11,321 k		8,880	14,598	12,005	13,079
	8,001	11,712	11,196	11,321		10,052	12,713	11,028	11,712
	9,731	10,052	10,345	11,028		8,927	11,712		13,079
	10,163	12,946		11,128 k		8,903			14,231
aver.	9,990	11,998	11,717	11,175	aver.	9,636	13,026	12,168	12,645
stdev.	1,263	1,242	1,250	0,207	stdev.	1,114	1,197	1,229	1,232